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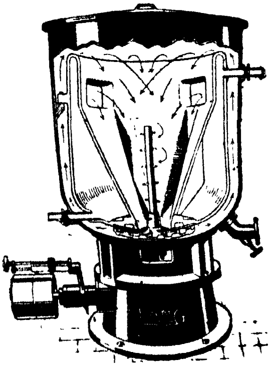

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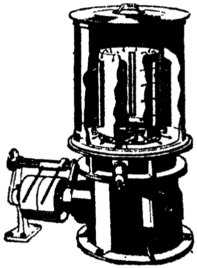

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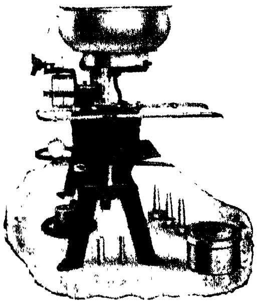

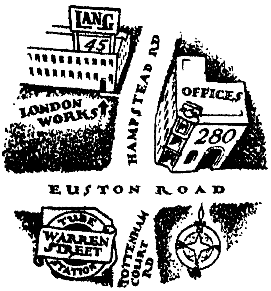

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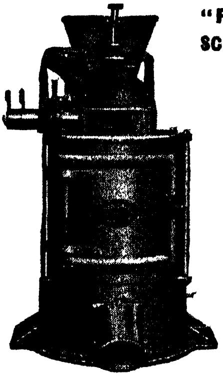

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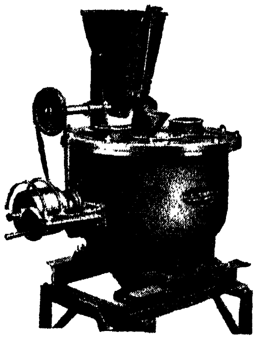

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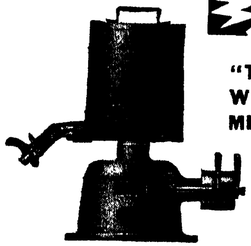

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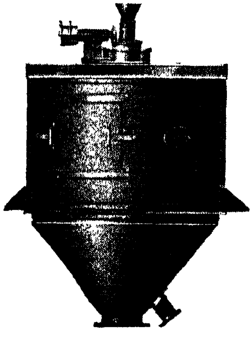

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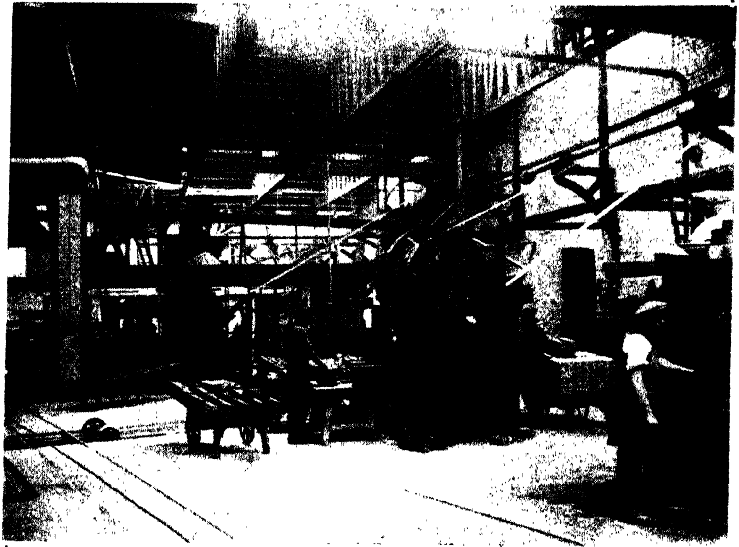

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Abbreviated Title.	Full Title.
A.	Abstracts in Journal of the Chemical Society (until 1925) or in British Chemical Abstracts,* Section A.
Acta Brev. Néerl.	Acta Brevia Néerlandica de Physiologia, Pharmacologia, Microbiologia, etc.
Acta Med. Scand.	Acta Medica Scandinavica.
Acta Phytochim.	Acta Phytochimica.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Amer. Soc. Testing Materials	American Society for Testing Materials.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Farm. Bioquím.	Anales de Farmacia y Bioquímica (Buenos Aires).
Anal. Fís. Quím.	Anales de la Sociedad Española Física y Química.
Analyst	The Analyst.
Angew. Chem.	Angewandte Chemie (formerly Zeitschrift für angewandte Chemie).
Anilinokras. Prom.	Anilinokrasotschnaja Promischlennosti.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. agron.	Annales agronomiques.
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Bot.	Annals of Botany.
Ann. Chim. appl.	Annali di Chimica applicata.
Ann. Falsif.	Annales des Falsifications et des Fraudes.
Ann. Inst. Pasteur	Annales de d'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. Reports	Annual Reports of the Chemical Society.
Ann. Soc. sci. Bruxelles	Annales de la Société scientifique de Bruxelles.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Mikrobiol.	Archiv für Mikrobiologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Phys. biol.	Archives de Physique biologique et de Chimie-physique des Corps organisés.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arch. Suikerind. Ned.-Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Atti R. Accad. Lincei	Atti (Rendiconti) della Reale Accademia Nazionale dei Lincei, classe di scienze fisiche, matematiche e naturali, Roma.
B.	British Chemical Abstracts,* Section B.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft.
Ber. physikal. Ges.	Berichte der deutschen physikalischen Gesellschaft.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Biol. Zentr.	Biologisches Zentralblatt.
Bot. Gaz.	The Botanical Gazette.
Brit. J. Exp. Biol.	British Journal of Experimental Biology (now The Journal of Experimental Biology).
Bul. Soc. Ştiinţe Cluj	Buletinul Societatie de Ştiinţe din Cluj.
Bull. Acad. roy. Méd. Belgique	Bulletin de l'Académie royale de Médecine de Belgique.

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* The year is not inserted in references to 1934.

Abbreviated Title.	Full Title.
Bull. Acad. Sci. U.R.S.S.	Bulletin de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Bull. Amer. Physical Soc.	Bulletin of the American Physical Society.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Inst. Min. Met.	Bulletin of the Institution of Mining and Metallurgy.
Bull. Inst. Phys. Chem. Res. Japan	Bulletin of the Institute of Physical and Chemical Research, Japan.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bur. Stand. J. Res.	Bureau of Standards Journal of Research.
Canadian J. Res.	Canadian Journal of Research.
Cellulosechem.	Cellulosechemie.
Chem. and Ind.	Chemistry and Industry.
Chem. Eng. Min. Rev.	Chemical Engineering and Mining Review.
Chem. Fabr.	Die Chemische Fabrik.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vědu a Průmysl."
Chem. Reviews	Chemical Reviews.
Chem. Weekblad.	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem.-Ztg.	Chemiker-Zeitung.
Coll. Czech. Chem. Comm.	Collection of Czechoslovak Chemical Communications.
Comm. Phys.-math. Soc. Sci. Fennica	Commentationes Physico-mathematicae (Societas Scientiarum Fennica).
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Acad. Sci. U.R.S.S.	Comptes rendus de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biology.
Compt. rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
Contr. Boyce Thompson Inst.	Contributions from the Boyce Thompson Institute.
Current Sci.	Current Science.
Dansk Tidsskr. Farm.	Dansk Tidsskrift for Farmaci.
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
Deut. Zuckerind.	Die Deutsche Zuckerindustrie.
Ergeb. exakt. Naturwiss.	Ergebnisse der exakten Naturwissenschaften.
Ernähr. Pflanze	Die Ernährung der Pflanze.
Fermentforsch.	Fermentforschung.
Fettchem. Umschau	Fettchemische Umschau.
Flora	Flora oder allgemeine botanische Zeitung.
Gazzetta	Gazzetta chimica italiana.
Hawaiian Planters Rec.	Hawaiian Sugar Planters' Association Records.
Helv. Chim. Acta	Helvetica Chimica Acta.
Helv. Physica Acta	Helvetica Physica Acta.
Ind. chim.	L'Industria chimica, mineraria e metallurgica.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind. Eng. Chem. (Anal.)	Industrial and Engineering Chemistry: Analytical Edition.
Indian J. Agric. Sci.	Indian Journal of Agricultural Science.
Indian J. Physics	Indian Journal of Physics.
J.	Journal of the Chemical Society.
J. Acoust. Soc.	Journal of the Acoustical Society of America.
J. Agric. Chem. Soc. Japan	Journal of the Agricultural Chemical Society of Japan.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	The Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.

Abbreviated Title.	FULL TITLE.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agronomy	Journal of the American Society of Agronomy.
J. Appl. Chem. Russia.	Journal of Applied Chemistry, Russia (Žhurnal prikladnoi Chimii).
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Bact.	Journal of Bacteriology.
J. Biochem. Japan.	Journal of Biochemistry, Japan.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Physics	The Journal of Chemical Physics.
J. Chim. physique	Journal de Chimie physique.
J. Chinese Chem. Soc.	Journal of the Chinese Chemical Society.
J. Clin. Invest.	The Journal of Clinical Investigation.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Chem. (*Russia*)	Journal of General Chemistry (U.S.S.R.) (formerly chemical part of the Journal of the Physical and Chemical Society of Russia).
J. Gen. Physiol.	Journal of General Physiology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry (now Industrial and Engineering Chemistry).
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Inst. Metals	Journal of the Institute of Metals.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute.
J. Landw.	Journal für Landwirtschaft.
J. Nutrition	Journal of Nutrition.
J. Oil and Col. Chem. Assoc.	Journal of the Oil and Colour Chemists' Association.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).
J. Physiol.	Journal of Physiology.
J. Phys. Radium	Journal de Physique et le Radium.
J. Physical Chem.	The Journal of Physical Chemistry.
J. Pomology	Journal of Pomology and Horticultural Science.
J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Roy. Soc. N.S.W.	Journal and Proceedings of the Royal Society of New South Wales.
J. Sci. Instr.	Journal of Scientific Instruments.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry, Japan (Kōgyō Kwagaku Zasshi).
Jahrb. wiss. Bot.	Jahrbuch für wissenschaftliche Botanik.
Japan. J. Physics	Japanese Journal of Physics.
K. Norske Vidensk. Selsk.	Kongelige Norske Videnskabers Selskabs (Forhandlingar).
Klin. Woch.	Klinische Wochenschrift.
Kolloid-Beih.	Kolloid-Beihefte.
Kolloid-Z.	Kolloid-Zeitschrift.
Korrosion u. Metallschutz	Korrosion und Metallschutz unter Einbeziehung des allgemeinen Materialschutzes.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Magyar Gyóg. Társas. Ért.	Magyar Gyógyszerésztudományi Társaság Értesitöje.
Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Manchester Lit. Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mem. R. Accad. d'Italia Sci. fis.	Memorie della reale Accademia d'Italia. Classe di Scienze fisiche, mathematiche e naturali.
Mercks Jahresber.	Mercks Jahresbericht.
Metallwirt.	Metallwirtschaft, Metallwissenschaft, Metalltechnik.

Abbreviated Title.	FULL TITLE.
Mikrochem.	Mikrochemie.
Metal Ind.	The Metal Industry.
Minnesota Agric. Exp. Sta. Tech. Bull.	Minnesota Agricultural Experiment Station Technical Bulletins.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nach. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Naturwiss.	Die Naturwissenschaften.
New Phytol.	New Phytologist.
New Zealand J. Sci. Tech.	New Zealand Journal of Science and Technology.
Nuovo Cim.	Il Nuovo Cimento.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Pharm. Ztg.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Physiol. Reviews	Physiological Reviews.
Phytopath.	Phytopathology.
Planta	Zeitschrift für wissenschaftliche Biologie. Abteilung E. Planta. Archiv für wissenschaftliche Botanik.
Plant Physiol.	Plant Physiology.
Polish Agric. Forestal Ann.	Polish Agricultural and Forestal Annual.
Proc. Amer. Acad. Sci.	Proceedings of the American Academy of Arts and Sciences.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. 4th Cong. Int. Soc. Sugar-Cane Bull.	Proceedings of the 4th Congress of the International Society of Sugar-Cane Technologists (Bulletin).
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy of Japan.
Proc. 2nd Internat. Cong. Soil Sci.	Proceedings of the 2nd International Congress of Soil Science.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam.
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Phys.-Math. Soc. Japan	Proceedings of the Physico-Mathematical Society of Japan.
Proc. Roy. Inst.	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Quart. J. Med.	Quarterly Journal of Medicine.
Rec. Trav. bot. néerl.	Recueil des Travaux botaniques néerlandais.
Rec. trav. chim.	Recueil des travaux chimiques Pays-Bas et de la Belgique.
Rend. R. Ist. Lombardo Sci. Lett.	Rendiconti dell' Reale Istituto Lombardo di Scienze e Lettere.
Rep. Brit. Assoc.	Reports of the British Association for the Advancement of Science.
Rev. Mod. Physics	Reviews of Modern Physics.
Rev. Sci. Instr.	Review of Scientific Instruments.
Rev. Trav. Office Pêches Maritimes	Revue des Travaux de l'Office des Pêches Maritimes.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.

Abbreviated Title.	FULL TITLE.
Sci. Papers Inst. Phys. Chem. Res. Tokyo.	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Rep. Nat. Tsing Hua Univ.	Science Reports of the National Tsing Hua University.
Sitzungsber. bayr. Akad. Wiss.	Sitzungsberichte der mathematisch-physikalischen Klasse der bayerischen Akademie der Wissenschaften zu München.
Sitzungsber. Heidelberg. Akad. Wiss.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Soil Sci.	Soil Science.
Suomen Kem.	Suomen Kemistilehti Acta Chemica Fennica.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
U.S. Hyg. Lab. Bull.	United States Hygienic Laboratory Bulletins.
U.S. Pub. Health Rep.	United States Public Health Service : Public Health Reports.
Ukrain. Chem. J.	Ukrainian Chemical Journal (Ukrainskiĭ Khemichniĭ Zhurnal).
Univ. California Pub. Physiol.	University of California Publications in Physiology.
Verhandl. deut. physikal. Ges.	Verhandlungen der deutschen physikalischen Gesellschaft.
Wien. klin. Woch.	Wiener klinische Wochenschrift.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie (now Angewandte Chemie).
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol.	Zeitschrift für Biologie.
Z. Bot.	Zeitschrift für Botanik.
Z. Elektrochem.	Zeitschrift für Elektrochemie (und angewandte physikalische Chemie).
Z. Krist.	Zeitschrift für Kristallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Pflanz. Düng.	Zeitschrift für Pflanzenernährung und Düngung.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. Unters. Lebensm.	Zeitschrift für Untersuchung der Lebensmittel.
Zavod. Lab.	Zavodskaya Laboratoriya.

ERRATA.

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Page	Line	
186	14	*for* " *iso*amylamine " *read* " *iso*amylaniline."
,,	4*	*for* " (XXVIII) " *read* " *p*-amino*iso*amylbenzene."

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* From bottom.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

1. THE HEAVY ISOTOPE OF HYDROGEN.

No apology is necessary for devoting a whole section to one element in view of the fundamental theoretical interest of molecules containing the new isotope and its great possibilities for use as an indicator in the physical and chemical behaviour of hydrogen compounds. Nearly 200 papers have appeared in this field during 1934, and the present report will be chiefly confined to indicating the directions in which work is being carried out, without discussing in any detail the theoretical points involved. As regards nomenclature, the name "deuterium" seems to be gaining favour in Europe as well as in America, and it will be used in this report. It is adopted in the Journal of the Chemical Society.

"Heavy water," or deuterium oxide, is no longer a chemical curiosity, but can now be bought in both continents either in the pure state or mixed with various proportions of H_2O. The electrolytic method of separation is still the only one used in practice, and a number of accounts of detailed procedure have been published.[1] The use of nickel cathodes in sodium hydroxide is usual, but alternative combinations are lead electrodes in sulphuric acid[2] and nickel in sodium sulphate solution.[3] The theory of the electrolytic separation will be dealt with later in this report.

The ratio D : H in naturally occurring water is dealt with elsewhere in these Reports.[4] The ratio in water from different sources, which is of great interest from the point of view of the production of the heavy isotope and the mechanism of the processes by which the water is formed, has been the subject of several researches, all of which rely on density measurements, and in view of the very small differences of density involved, it is important to purify the water very thoroughly, and also to avoid fractionation on distillation. M. Dole [5] found that this error invalidated his earlier work [6] on the water derived from benzene, kerosene, and honey. A large number of specimens of water of mineral, vegetable, animal, and industrial origin have been examined by E. W. Washburn and Smith,[7] and by a team of workers at the Imperial College, using elaborate precautions.[8] The latter authors claim a relative accuracy of 2 parts per million in the isotopic ratio. Most of the natural samples were found to contain more deuterium than ordinary tap water, which is probably due to evaporation. No significant variations were found for the same type of water at different points of the earth's surface. In agreement with other authors, they find that the crystallisation of salts from water causes no displacement of the isotopic ratio.[9] On the other hand, fractional freezing was found to give rise to a small separation, which may account for differences previously reported in the densities of natural and artificial ice. There is, however, some dispute as to the facts: while E. S. Gilfillan [10] also finds a separation, G. Bruni [11] obtained negative results on repeating his former work with M. Strada.[12] The disagreement about these experiments carried out with pure water shows the need for caution in accepting results obtained with water from biological sources.

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[1] P. Harteck, *Proc. Physical Soc.*, 1934, **46**, 277; *A.*, 236; H. S. Taylor, H. Eyring, and A. A. Frost, *J. Chem. Physics*, 1933, **1**, 823; *A.*, 1934, 154; L. C. Anderson, J. O. Halford, and J. R. Bates, *ibid.*, 1934, **2**, 342; *A.*, 851; K. Schwarz, L. Küchler, and H. Steiner, *Z. Elektrochem.*, 1934, **40**, 298; *A.*, 852.

[2] L. Tronstad and J. Brun, *ibid.*, p. 556; *A.*, 1077; T. Titani, K. Kurano, and M. Harada, *Bull. Chem. Soc. Japan*, 1934, **9**, 269; *A.*, 1077.

[3] *Idem*, *ibid.*, p. 272; *A.*, 1077.

[4] P. 98.

Very pure D_2 has been obtained by diffusion.[13] Observation of the atomic spectra of the isotopes of hydrogen provides a very direct test of the effect of the nuclear mass on the electronic spectra. Such measurements have been carried out by a number of workers,[14] and the small shifts observed are in complete agreement with the theory. Effects of much greater magnitude and complexity are observed in the molecular spectra of hydrogen and its compounds. To a very good approximation we may regard the potential-energy curves as being unchanged,[15] and it is then an easy matter to calculate (for a diatomic molecule) the effect of replacing H by D on the energy of the vibrational states, while the rotational states are affected only by the change in the moment of inertia. Taking into account the fact that a mixture of the two isotopes contains the species H_2, D_2, and HD, all the features of the vibration–rotation spectrum can be predicted, and the results obtained agree well with the predictions.[16] In the case of the D_2 molecule alternations in the intensity of the rotational spectrum reveal the presence of ortho- and para-modifications, and show that the nuclear spin of the deuton is 1, *i.e.*, twice that of the proton.[17] Similar calculations can be carried out for other diatomic molecules containing deuterium, *e.g.*, DCl,[18] AlD,[19] and OD.[20] The interpretation of the isotope effects in the spectra of molecules containing more than two atoms is more difficult, but it is just in these cases that valuable information may be obtained. The replacement of H by D represents a change in mass without any change in the force constants or other characteristics of the molecule, and may thus be regarded as a new independently variable parameter. In many molecules the partial replacement reduces the symmetry in such a way as to increase the number of observable frequencies, *e.g.*, in the case of CH_4 and CH_3D.[21] A number of other compounds have been investigated.[22]

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[5] *J. Chem. Physics*, 1934, **2**, 548; *A.*, 1185.

[6] *Ibid.*, p. 337; *A.*, 853.

[7] *Science*, 1934, **79**, 188.

[8] H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell, and H. V. A. Briscoe, *J.*, 1934, 1207, 1948; *A.*, 1080.

[9] H. Erlenmeyer and H. Gärtner, *Nature*, 1934, **134**, 327; *A.*, 1080; J. A. N. Friend, *ibid.*, p. 463; *A.*, 1062.

[10] *J. Amer. Chem. Soc.*, 1934, **56**, 2201; *A.*, 1317.

[11] *Ibid.*, p. 2013; *A.*, 1185.

[12] *Atti R. Accad. Lincei*, 1934, [vi], **19**, 453; *A.*, 1080.

[13] H. Harmsen, G. Hertz, and W. Schütze, *Z. Physik*, 1934, **90**, 703; *A.*, 1185.

[14] D. H. Rank, *Physical Rev.*, 1932, [ii], **42**, 446; *A.*, 1933, 1219 (γ line); R. C. Williams and R. C. Gibbs, *ibid.*, 1934, [ii], **45**, 475; *A.*, 575 (fine structure of H_α and D_α); J. K. Robertson, *Nature*, 1934, **134**, 378; *A.*, 1147 (Balmer lines); J. S. Foster and A. H. Snell, *ibid.*, p. 568; *A.*, 575 (Stark effect).

The spectroscopic data are sufficiently well established to allow a complete calculation of the equilibrium properties of a gaseous mixture containing given proportions of H and D. The properties calculated include the equilibrium constant for the reaction

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[15] This is not justified for very refined calculations: see *e.g.*, R. L. de Kronig, *Physica*, 1934, 1, 617; *A.*, 826.

[16] See, *e.g.*, G. H. Dieke and R. W. Blue, *Nature*, 1934, **133**, 601; *A.*, 575.

[17] G. M. Murphy and (Miss) H. Johnston, *Physical Rev.*, 1934, [ii], **46**, 95; *A.*, 1051; G. N. Lewis and (Miss) M. Ashley, *ibid.*, 1933, **43**, 857.

[18] J. H. Hardy, E. F. Barker, and D. M. Dennison, *ibid.*, 1932, [ii], **42**, 279; *A.*, 1933, 6.

[19] W. Holst and E. Hulthén, *Nature*, 1934, **133**, 496; *A.*, 472.

[20] H. L. Johnston and D. H. Dawson, *Naturwiss.*, 1933, **21**, 495; *A.*, 1933, 763.

[21] E. F. Barker and N. Ginsburg, *J. Chem. Physics*, 1934, **2**, 299; *A.*, 716.

[22] See, *e.g.*, E. Bartholomé and K. Clusius, *Z. Elektrochem.*, 1934, **40**, 529; *A.*, 941; J. W. Ellis and B. W. Sarge, *J. Chem. Physics*, 1934, **2**, 559; *A.*, 1154 (D_2O and HDO); A. McKellar and C. A. Bradley, *Physical Rev.*, 1934, **46**, 664; *A.*, 1288 (C_2HD); G. B. B. M. Sutherland, *Nature*, 1934, **134**, 775; *A.*, 1935, 10. See also next section of this report.

$H_2 + D_2 \rightleftharpoons 2HD$,[23] the equilibrium between ortho- and para-H_2 and ortho- and para-D_2,[24] the equilibrium between atoms and molecules,[25] and the specific heat.[26] The experimental values are in all cases in agreement with the values calculated from the spectroscopic data. Determinations of the specific heat by means of the hot-wire method may be used to determine the amounts of H_2, D_2, and HD present in any sample of hydrogen.[27]

The same considerations can be applied to other chemical equilibria involving the hydrogen isotopes; *e.g.*, it is found, as predicted,[28] that the degree of thermal dissociation of DI differs from that of HI by about 6% at 468°.[29] There are two principal ways in which the theoretical expression for the equilibrium constant of such a reaction involves the mass; first, in the zero-point energy, and secondly, in the chemical constant. These factors act in opposite directions, and approximately balance for most pairs of isotopes, but they may give rise to considerable differences in the case of the hydrogen isotopes. For molecules containing more than one hydrogen atom, the partial replacement of H by D will also change the symmetry number contained in the chemical constant, and thus will affect the equilibrium. This is the case for the reaction $H_2 + HDO \rightleftharpoons H_2O + HD$, which is of great practical importance. In this case the interpretation of the spectra in terms of energy states is not quite complete; nevertheless, the experimental measurements of this equilibrium are in good accord with the calculations from spectroscopic data.[30] At room temperature this reaction has an equilibrium constant of about 3·8, compared with the "classical" value of unity. It is possible that equilibria which differ greatly for the two isotopes may eventually displace the electrolytic method as a source of deuterium compounds.[31]

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[23] D. Rittenberg, W. Bleakney, and H. C. Urey, *J. Chem. Physics*, 1934, **2**, 48; *A.*, 237; A. Farkas and L. Farkas, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 467; *A.*, 608; A. J. Gould, W. Bleakney, and H. S. Taylor, *J. Chem. Physics*, 1934, **2**, 367; *A.*, 1074.

[24] A. Farkas, L. Farkas, and P. Harteck, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 481; *A.*, 608; H. Motz and F. Patat, *Monatsh.*, 1934, **64**, 17; *A.*, 480.

[25] H. L. Johnston and E. A. Levy, *J. Chem. Physics*, 1934, **2**, 389; *A.*, 951.

[26] K. Clusius and E. Bartholomé, *Naturwiss.*, 1934, **22**, 297; *A.*, 722; *Z. Elektrochem.*, 1934, **40**, 524; *A.*, 951.

[27] A. Farkas and L. Farkas, *loc. cit.*, ref. (23).

[28] See *Ann. Reports*, 1933, **30**, 32.

[29] D. Rittenberg and H. C. Urey, *J. Amer. Chem. Soc.*, 1934, **56**, 1885; *A.*, 1172.

[30] R. H. Crist and G. A. Dalin, *J. Chem. Physics*, 1934, **2**, 442, 735; *A.*, 962; L. Farkas and A. Farkas, *Trans. Faraday Soc.*, 1934, **30**, 1071; *A.*, 1935, 33; T. Förster, *Z. physikal. Chem.*, 1934, **27**, [*B*], 1, 319; *A.*, 1935, 33.

[31] See M. Polanyi, *Nature*, 1935, in the press.

A number of other equilibrium properties of deuterium and its compounds have been measured. Many of these admit of no quantitative interpretation, but it is often possible to make interesting qualitative comparisons between the " heavy " and " light " compounds. A number of workers have studied the thermal properties of liquid and solid D_2.[32] The boiling point is 23·5° K. and the triple point 18·6° K. Comparisons of vapour pressure have been made for DCl and HCl and for DCN and HCN by G. N. Lewis, R. T. Macdonald, and P. W. Schutz,[33] and for DF and HF by W. H. Claussen and J. H. Hildebrand.[34] Only small differences were observed ; this is particularly interesting for HF and DF, since differences due to different degrees of association (as for H_2O and D_2O) might have been anticipated. The refractive index, freezing point, density, and viscosity of pure liquid D_2O have been measured,[35] giving values differing somewhat from those previously accepted.[36] The ionic product of D_2O has been found to be about one-third that of H_2O at the same ionic concentration.[37] The dissociation constants of a few weak electrolytes (containing D in place of H) have been measured in D_2O, giving results considerably lower than the corresponding values in H_2O.[38] On diluting D_2O with H_2O, heat is absorbed, indicating that there are stronger intermolecular forces (greater association) in the former than in the latter.[39] DHO diffuses into H_2O with an abnormally great velocity, presumably due to some chain mechanism such as that postulated to explain the mobility of the hydrogen ion.[40]

To the physical chemist, special interest centres round the differences in reaction velocity between hydrogen compounds and the corresponding deuterium compounds. As pointed out in last year's Report,[41] the determining factor in many cases will be the difference in zero-point energy in the initial states, which will in general lead to a higher activation energy (and hence a lower reaction velocity) for the deuterium compounds. It has been noted by M. Polanyi[42] that in some cases (especially for reactions of free atoms) this state of affairs may be reversed by the difference of zero-point energies in the activated complex. Another way in which the difference of mass may lead to differences in reaction velocity is in the behaviour of the particles in crossing the potential barrier. For heavy atoms this process can be described in terms of classical mechanics, but for H and D the wave nature of the particles must be taken into account,[43] and calculation shows that at not too high temperatures this effect alone may lead to considerable differences between the isotopes.[44] Finally, small differences may also be caused by the differences in thermal velocity. It is thus difficult to produce any complete explanation of the experimental data, but in a number of cases the facts seem to be qualitatively explicable in terms of the differences in zero-point energy alone. L. Farkas and A. Farkas[45] find that D_2 reacts with chlorine one-third as fast as H_2 in the photochemical chain reaction, and attribute this to the initial reaction $D_2(H_2) + Cl \longrightarrow DCl(HCl) + D(H)$. H. W. Melville[46] has investigated the reaction of H and D atoms and molecules with oxygen, nitrous oxide, ethylene, acetylene, and carbon monoxide. When the atoms react in the gas phase, the only differences observed can be attributed to differences in collision frequency, but when molecules take part, differences attributable to zero-point energies are observed, and the same is true for the reaction of atoms adsorbed on a surface. None of the data indicated that the "leakage" of the atoms through potential barriers was an appreciable factor. The reaction between deuterium and oxygen has also been investigated.[47] The change in the upper pressure limit can be accounted for by the different deactivating powers of H_2 and D_2, owing to their different molecular velocities, the velocities of the actual branching processes being substantially the same. The surface reaction is about 1·6 times slower for D_2 than for H_2: after allowing for the different diffusion coefficients, this can be accounted for by the differences in the zero-point energies of the two molecules. The rates of diffusion of the two isotopes through palladium can be explained on the same basis.[48] Other gas reactions which have been studied are $D_2 + Br_2$[49] and $C_2H_4 + HD$;[50] in the latter case the two reactions $C_2H_4 + HD \longrightarrow C_2H_3D + H_2$ and $C_2H_4 + HD \longrightarrow C_2H_5D$ take place simultaneously. In the heterogeneous hydrogenation of ethylene the velocity–temperature curves for H_2 and D_2 cross; this is probably due to the greater adsorption of the latter.[51] The kinetics of the reaction $H_2 + D_2 \rightleftharpoons 2HD$ are complex, and probably involve the separate homogeneous reactions $H_2 + D \rightleftharpoons HD + D$, $D_2 + H \rightleftharpoons HD + H$, and $H_2 + D_2 \rightleftharpoons 2HD$.[52]

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[32] K. Clusius and E. Bartholomé, *Naturwiss.*, 1934, **22**, 526; *A.*, 1062; G. N. Lewis and W. T. Hanson, *J. Amer. Chem. Soc.*, 1934, **56**, 1687; *A.*, 1062; R. B. Scott, F. G. Brickwedde, H. C. Urey, and M. H. Wahl, *J. Chem. Physics*, 1934, **2**, 454; *A.*, 1164.

[33] *J. Amer. Chem. Soc.*, 1934, **56**, 494, 1001; *A.*, 355, 590.

[34] *Ibid.*, p. 1820; *A.*, 1062.

[35] H. S. Taylor and P. W. Selwood, *ibid.*, p. 998; *A.*, 590.

[36] Cf. *Ann. Reports*, 1933, **30**, 31.

[37] B. Topley and W. F. K. Wynne-Jones, *Nature*, 1934, **134**, 574; *A.*, 1173; E. Abel, E. Bratu, and O. Redlich, *Z. physikal. Chem.*, 1934, **170**, 153; *A.*, 1173.

[38] G. N. Lewis and P. N. Schutz, *J. Amer. Chem. Soc.*, 1934, **56**, 1913; *A.*, 1173.

[39] E. Doehlemann, E. Lange, and H. Voll, *Naturwiss.*, 1934, **22**, 526; *A.* 1071.

[40] W. J. C. Orr and D. W. Thompson, *Nature*, 1934, **134**, 776.

[41] *Ann. Reports*, 1933, **30**, 32.

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[42] *Nature*, 1934, **133**, 26; *A.*, 150.

[43] R. P. Bell, *Proc. Roy. Soc.*, 1933, [*A*], **139**, 466; *A.*, 1933, 231.

[44] C. E. H. Bawn and G. Ogden, *Trans. Faraday Soc.*, 1934, **30**, 432; *A.*, 602; R. P. Bell, *Proc. Roy. Soc.*, in the press.

[45] *Naturwiss.*, 1934, **22**, 218; *A.*, 603.

[46] *Nature*, 1934, **133**, 947; *A.*, 847; *J.*, 1934, 797, 1243; *A.*, 851, 1078.

[47] C. N. Hinshelwood, A. T. Williamson, and J. H. Wolfenden, *Nature*, 1934, **133**, 836; *A.*, 736; *Proc. Roy. Soc.*, 1934, [*A*], **147**, 48; *A.*, 1935, 39; A. A. Frost and H. N. Alyea, *J. Amer. Chem. Soc.*, 1934, **56**, 1251; *A.*, 736; K. Clusius and H. Gutschmidt, *Naturwiss.*, 1934, **22**, 693; *A.*, 1178.

A number of reaction velocities have been compared in H_2O and D_2O. The same general principles will of course apply, but the theoretical treatment is complicated by the change of medium and the possibility of interchange between solvent and solute. Most of the reactions studied have been of the catalytic type. The mutarotation of glucose has been studied by E. Pascu,[53] E. A. Moelwyn-Hughes, R. Klar, and K. F. Bonhoeffer,[54] W. F. K. Wynne-Jones,[55] and V. K. LaMer and W. H. Hamill.[56] With $H_3O^{\bullet}$ and $D_3O^{\bullet}$ as catalysts, the ratio of the velocities at room temperature is about 1·3 : 1 and the differences in the activation energies 1250 cals. For catalysis by the solvents H_2O and D_2O the ratio of the velocities is about 3·8 : 1 and the difference in the activation energies (after correction for the temperature coefficient of viscosity) 550 cals. The differences in velocity are in each case accounted for by the differences in activation energy and viscosity. The inversion of sucrose catalysed by $H_3O^{\bullet}$ and $D_3O^{\bullet}$ has also been studied by a number of authors.[57] The somewhat surprising fact emerges that the velocity of inversion in D_2O is nearly twice as great as in H_2O;

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[48] A. Farkas and L. Farkas, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 467; *A.*, 608.

[49] K. F. Bonhoeffer, F. Bach, and E. Fajans, *Z. physikal. Chem.*, 1934, **168**, 313; *A.*, 736.

[50] A. Farkas, L. Farkas, and E. K. Rideal, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 630; *A.*, 1315.

[51] R. Klar, *Z. physikal. Chem.*, 1934, **27**, [*B*], 319.

[52] E. K. Rideal, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 481.

[53] *J. Amer. Chem. Soc.*, 1934, **56**, 745; *A.*, 494.

[54] *Z. physikal. Chem.*, 1934, **169**, 113; *A.*, 971; *ibid.*, 1934, **26**, [*B*], 272; *A.*, 1075.

[55] *J. Chem. Physics*, 1934, **2**, 381; *A.*, 1075.

[56] *Ibid.*, p. 891.

[57] E. A. Moelwyn-Hughes and K. F. Bonhoeffer, *Naturwiss.*, 1934, **22**, 174; P. Gross, H. Suess, and H. Steiner, *ibid.*, 1934, **22**, 662; *A.*, 1180; Moelwyn-Hughes, *loc. cit.*, ref. (54).

however, this may be explained by assuming that the sucrose–$D^{\cdot}$ complex is formed to a greater extent than the sucrose–$H^{\cdot}$ complex. It may be noted that the enzymatic inversion of sucrose is somewhat slower in D_2O than in H_2O.[58]

Wynne-Jones [55] has measured the rate of neutralisation of nitroethane by baryta in H_2O and by $Ba(OD)_2$ in D_2O. He concludes that under the same conditions the rate of transfer of protons is at least 10 times that for deutons, and the rate of transfer of $H^{\cdot}$ to OD' in D_2O is about 50% greater than its rate of transfer to OH' in H_2O.

The discharge of the two isotopes of hydrogen by metals, with or without the application of an electric field, constitutes a special problem in reaction kinetics. The preferential discharge of H in electrolysis is, of course, the basis of the usual method of separation, and it is found that the chemical dissolution of metals in water containing both H and D always leads to preferential liberation of the former.[59]

The theory of these processes is at present very uncertain; theoretical treatments from different points of view have been given, but there is not yet sufficient experimental evidence to discriminate between the different possible mechanisms.[60] The electrolytic separation coefficient is not greatly affected by change of electrode metal or current density,[61] but occasionally acquires abnormally low values, *e.g.*, with activated platinum electrodes.[62] This is probably due to the partial establishment of the equilibrium $HD + H_2O \rightleftharpoons H_2 + HDO$, catalysed by the metal;[63] this factor makes it difficult to conclude anything about the primary products of the electrolysis, and may account for some of the erratic results which have been obtained.

The heavy isotope of hydrogen has already been used in a number of cases for detecting and measuring the interchange of hydrogen between different substances. The theoretical implications of the results obtained are so varied that we can do no more here than report the facts. Hydrogen gas does not interchange with water at ordinary temperatures except in presence of a catalyst,[64] in contradiction to the previous observation of M. L. Oliphant.[65] No interchange takes place between water and potassium acetate, benzoate, or hypophosphite, but ethylene glycol immediately exchanges one-third of its hydrogen.[66] Between acetone and water, exchange is extremely slow in neutral solution, more rapid in acid solution, and still more rapid in alkaline solution; all six hydrogens are exchanged.[67] There is also slow interchange with acetaldehyde, formaldehyde, and acetal.[68] Acetylene and water exchange in presence of alkali, but not in pure water or phosphoric acid solution.[69] Benzene and water interchange in the presence of platinum-black [70] and of sulphuric acid.[71] It is hardly necessary to point out the immense possibilities of work of this kind, particularly from the point of view of the reactivity of hydrogen atoms in organic compounds and the theory of both homogeneous and heterogeneous catalysis.

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[58] E. W. R. Steacie, *Z. physikal. Chem.*, 1934, **27**, [*B*], 1.

[59] E. D. Hughes, C. K. Ingold, and C. L. Wilson, *J.*, 1934, 493; *A.*, 612; A. Farkas and L. Farkas, *Nature*, 1934, **133**, 139; *A.*, 264; J. Horiuti and A. L. Szabo, *ibid.*, p. 327; *A.*, 375; C. O. Davis and H. L. Johnston, *J. Amer. Chem. Soc.*, 1934, **56**, 492; *A.*, 375.

[60] M. Polanyi, *Naturwiss.*, 1933, **21**, 316; *A.*, 1933, 659; B. Topley and H. Eyring, *J. Chem. Physics*, 1934, **2**, 217; *A.*, 851; R. P. Bell, *ibid.*, p. 164; *A.*, 738; R. H. Fowler, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 452; *A.*, 609; C. E. H. Bawn and G. Ogden, *Trans. Faraday Soc.*, 1934, **30**, 432; *A.*, 602.

[61] R. P. Bell and J. H. Wolfenden, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 22.

[62] Topley and Eyring, *loc. cit.*, ref. (60).

[63] A. Farkas and L. Farkas, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 623; *A.*, 1315.

R. P. B.

2. THE RAMAN EFFECT.

Several relatively short references to the Raman effect have been made in previous Annual Reports.[1] The objects of the present Report are (1) to give a rather more connected account of some of the applications of the effect to problems of interest in chemistry and (2) to illustrate these applications by selected examples, with special regard to recent work. So large and varied is the literature (about a thousand papers have already appeared on the subject) that nothing like completeness is claimed on either score. A full bibliography from July 1930 to August 1932 inclusive has been compiled by S. C. Sirkar [2] to form a continuation of an earlier bibliography.[3] It is arranged under general subject headings and has an author index and a substance index.

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[64] A. J. Gould and W. Bleakney, *J. Amer. Chem. Soc.*, 1934, **56**, 247; *A.*, 264.

[65] See *Ann. Reports*, 1933, **30**, 33.

[66] N. F. Hall, E. Bowden, and T. O. Jones, *J. Amer. Chem. Soc.*, 1934, **56**, 750; *A.*, 497.

[67] K. Schwarz and H. Steiner, *Z. physikal. Chem.*, 1934, **24**, [*B*], 153; *A.*, 613; R. Klar, *Z. physikal. Chem.*, 1934, **26**, [*B*], 335; *A.*, 1080.

[68] R. Klar, *loc. cit.*, ref. (67).

[69] L. H. Reyerson and S. Yuster, *J. Amer. Chem. Soc.*, 1934, **56**, 1426; *A.*, 853.

[70] H. Horiuti, G. Ogden, and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 663; *A.*, 973.

[71] C. K. Ingold, C. G. Raisin, and C. L. Wilson, *Nature*, 1934, **134**, 734. For a discussion of the mechanism, see *idem*, also Horiuti and Polanyi, *ibid.*, p. 847.

[1] *Ann. Reports*, 1929, **26**, 16, 127, 286; 1931, **28**, 182, 284, 370; 1932, **29**, 23.

[2] *Indian J. Physics*, 1932, **7**, 431.

The Raman Effect in Chemical Analysis.—When monochromatic light of frequency ν_0 is scattered by a dust-free transparent substance (solid, liquid, or gas), the scattered spectrum in general contains (in addition to a line of unchanged frequency *) a number of relatively feeble new lines[4] of modified frequencies ν'. These so-called Raman lines are characterised by the fact that the magnitudes of the frequency shifts $\nu_0-\nu'$ (Raman frequencies) are independent of ν_0 and determined only by the nature of the scattering molecules. The experimental technique for photographing Raman spectra remains essentially similar to that described by K. W. F. Kohlrausch.[5]

Each different scattering molecular species gives its own characteristic Raman spectrum—writes (as it were) its autograph on the photographic plate. The most obvious application to chemistry, and one involving no knowledge whatever of the mechanism of the effect, is for the identification of different molecular species. The usefulness of the method becomes apparent in view of the facts that (1) the components of a mixture in general exert practically no effect on each other's Raman spectra [6] and (2) small differences of molecular structure may be associated with very marked differences of spectra. An advantage of the Raman effect over some other physical methods (*e.g.*, refractivity, Kerr effect, dipole moment, etc.) is that the spectra consist of lines and therefore remain discrete even when superimposed, so that the components of a mixture preserve a readily recognisable individuality. Both theory (see below) and experiment show, further, that for a given molecular species the intensity of the effect is directly proportional to the number of scattering molecules, *i.e.*, for constant volume is proportional to the concentration. Hence the Raman effect can be used for quantitative as well as for qualitative analysis. In this connexion, as in all the applications, the scope is limited by the feebleness of

[3] *Indian J. Physics*, 1931, **5**, 257.

[4] (Sir) C. V. Raman and K. S. Krishnan, *Nature*, 1928, **121**, 501; *A.*, 1928, 461; C. V. Raman, *Indian J. Physics*, 1928, **2**, 387; *A.*, 1928, 685; C. V. Raman and K. S. Krishnan, *ibid.*, p. 399; *A.*, 1928, 1075; G. Landsberg and L. Mandelstam, *Naturwiss.*, 1928, **16**, 557; *A.*, 1928, 936.

[5] "Der Smekal–Raman-Effekt," Springer, Berlin, 1931.

[6] See, *e.g.*, R. E. Whiting and W. H. Martin, *Trans. Roy. Soc. Canada*, 1931, [iii], **25**, III, 87; *A.*, 1932, 320; A. Dadieu and K. W. F. Kohlrausch, *Physikal. Z.*, 1929, **30**, 384; *A.*, 1929, 976; *ibid.*, 1930, **31**, 514; *A.*, 1930, 840.

[*] It has recently been shown (W. Ramm, *Physikal. Z.*, 1934, **35**, 756; *A.*, 346) that this line has a fine structure, being accompanied by others of very slightly modified frequency. These are due to a cause essentially different from that operative in the Raman effect, and will not be considered here.

the effect. However, it has been found possible to detect, *e.g.*, about 2% of unsaturated impurities in *cyclo*propane derivatives;[7] benzene–toluene mixtures can be analysed with an accuracy of about 5%;[8] and as little as 0·4% of styrene has been detected in ethylbenzene.[9] The Raman effect can be used where ordinary chemical methods are hardly applicable, *e.g.*, to detect *m*-xylene (down to 1%) in an *op*-mixture.[10] Amongst other applications may be mentioned the distinction between *cis-trans*[11] and other isomerides[12] and the study of degree of hydrolysis,[13] polymerisation,[14] formation of mixed molecules from phosphorus trichloride and tribromide,[15] molecular structure of nitrobenzene above and below its transition temperature (no evidence of difference being found),[16] complexity of the mercurous ion in solution,[17] and velocity of *cis-trans*-change[18] and of esterification.[19]

Special interest attaches to the study of the degree of ionisation of electrolytes in solution by means of the Raman effect. The method makes it possible to distinguish between ions and unionised molecules and to follow quantitatively the changes in the equilibrium between them as the concentration is altered. Reference has already been made[20] to this work, which has shown that nitric and sulphuric acids are only partly ionised in water at moderate concentrations. These results have subsequently been confirmed by more detailed studies of these acids.[21] Hydrochloric acid, which appears to be practically completely ionised in aqueous solutions,[20] has been investigated in non-aqueous solvents and shown to be present as un-ionised molecules.[22] The magnitude of the frequency is found to depend upon the polar character of the solvent.

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[7] R. Lespieau, M. Bourguel, and R. L. Wakeman, *Compt. rend.*, 1931, **193**, 238; *A.*, 1931, 1147.

[8] (Miss) E. A. Crigler, *J. Amer. Chem. Soc.*, 1932, **54**, 4207; *A.*, 1933, 7.

[9] J. Weiler, *Verhandl. deut. physikal. Ges.*, 1932, **13**, 5.

[10] L. Birkenbach and J. Goubeau, *Ber.*, 1932, **65**, [*B*], 1140; *A.*, 1932, 954.

[11] O. Miller and L. Piaux, *Compt. rend.*, 1933, **197**, 412; *A.*, 1933, 998.

[12] M. Milone, *Gazzetta*, 1933, **63**, 456; *A.*, 1933, 1228; P. Lambert and J. Lecompte, *Compt. rend.*, 1934, **198**, 1316; *A.*, 583.

[13] P. Krishnamurti, *Indian J. Physics*, 1931, **6**, 345; *A.*, 1932, 228.

[14] S. Bhagavantam, *ibid.*, 1930, **5**, 49; *A.*, 1930, 1238.

[15] B. Trumpy, *Z. Physik*, 1931, **68**, 675; *A.*, 1931, 785.

[16] A. M. Thorne and P. L. Bayler, *Physical Rev.*, 1932, [ii], **41**, 376; *A.*, 1933, 1229; H. F. Hertlein, *Z. Physik*, 1934, **87**, 744; *A.*, 346.

[17] L. A. Woodward, *Phil. Mag.*, 1934, [vii], **18**, 823.

[18] H. Conrad-Billroth, K. W. F. Kohlrausch, and A. Pongratz, *Z. physikal. Chem.*, 1932, [*B*], **17**, 233; *A.*, 1932, 706.

[19] S. Partharasathy, *Phil. Mag.*, 1934, [vii], **17**, 471; *A.*, 369.

[20] *Ann. Reports*, 1932, **29**, 23.

[21] I. R. Rao, *Indian J. Physics*, 1933, **8**, 123; *A.*, 1934, 9; L. A. Woodward and R. G. Horner, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 129; *A.*, 473; R. M. Bell and M. A. Jeppeson, *J. Chem. Physics*, 1934, **2**, 711; *A.*, 1289; L. Médard, *Compt. rend.*, 1933, **197**, 582; *A.*, 1933, 1102; L. Médard and H. Volkringer, *ibid.*, p. 833; *A.*, 1933, 1228.

The Raman spectrum of water continues to receive attention, in both the vapour [23] and the liquid [24] state. In particular, I. R. Rao concludes, from a study of the intensity distribution in the Raman bands at different temperatures,[25] that the degree of polymerisation varies with temperature—a result which may be interpreted in terms of recent theories of liquid water.[26]

The power of the Raman effect as a method of chemical analysis is enhanced by the fact (see below) that many organic groups give rise to characteristic lines whose frequencies are more or less independent of the rest of the molecule. This makes it possible to use the phenomenon to detect the presence or absence, not only of molecular species in a mixture, but also of particular groups within a molecule (see further below). The spectra of germani-chloroform and stanni-chloroform may be quoted as an example. These are found [27] to be similar to that of chloroform except for the absence of a frequency attributable to the linking of the hydrogen atom. The explanation advanced is that ionisation may occur for the germanium and the tin compound.

Raman Effect and Restoring Forces in Molecules.—In the above applications, the " molecular autograph " is used merely for identification purposes, and no attempt is made to deduce character from the handwriting. The scope of application is widened by the observation [4] that many strong Raman frequencies are equal to fundamental vibration frequencies of the scattering molecule, as observed in infra-red absorption or emission.

The possibility of such changes of frequency had been foreseen as early as 1923 by A. Smekal,[28] who gave a simple interpretation in terms of the extreme quantum theory. A light quantum of energy $h\nu_0$ impinges on a molecule, gives up the energy $h\nu$ in setting the molecule vibrating with frequency ν, and is thereby scattered with the diminished energy $h\nu_0 - h\nu = h\nu'$. If the scattering molecule is originally vibrating, the incident quantum may pick up the energy $h\nu$ and have its frequency increased. The magnitude of the frequency shift (Raman frequency) is in either case ν.

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[22] W. West and P. Arthur, *J. Chem. Physics*, 1934, **2**, 215; *A.*, 583.

[23] D. H. Rank, *ibid.*, 1933, **1**, 504; *A.*, 1934, 10.

[24] G. Bolla, *Nuovo Cim.*, 1933, [ii], **10**, 101; *A.*, 1934, 10; I. M. Magat, *J. Phys. Radium*, 1934, [vii], **5**, 347; *A.*, 1055; J. Cabannes and J. de Riols, *Compt. rend.*, 1934, **198**, 30; *A.*, 238; I. R. Rao, *Z. Physik*, 1934, **90**, 658; *A.*, 1155.

[25] *Phil. Mag.*, 1934, [vii], **17**, 1113; *A.*, 829; *Proc. Roy. Soc.*, 1934, [*A*], **145**, 489; *A.*, 942; cf. G. B. B. M. Sutherland, *ibid.*, 1933, [*A*], **141**, 542; *A.*, 1933, 1103.

[26] See *Ann. Reports*, 1933, **30**, 34.

[27] H. Volkringer, A. Tchakirian, and (Mme.) M. Freymann, *Compt. rend.*, 1934, **199**, 292; *A.*, 942.

[28] *Naturwiss.*, 1923, **11**, 873.

Thus the Raman effect, with its relatively simple technique, provides a convenient method of photographing infra-red frequencies by means of visible or ultra-violet light. It must be noted that there is, in general, a lack of correspondence between infra-red and Raman spectra as far as number of lines, relative intensities, etc., are concerned; for it is not to be expected that the selection rules, etc. (see below), will be the same for such different processes. The two methods must be regarded as complementary; and to obtain the most complete information, corresponding infra-red and Raman spectra must be taken together. A notable feature of the latter is their relative simplicity, due to the fact (deducible from the complete theory—see below) that only fundamental vibration frequencies can occur strongly, harmonics and combination frequencies being relatively very weak. In the sequel we shall deal only with fundamentals.

In a comparatively few cases (molecules with small moments of inertia) it is possible to observe the rotational fine structure of vibrational Raman lines. Pure rotational Raman lines may also be observed on both sides of the line scattered without change of frequency. As with infra-red data, the rotational frequencies may be used to calculate the moments of inertia of the scattering molecules. Further than this, the complete theory of the intensity distribution, etc., of the rotational lines, as worked out by G. Placzek and E. Teller,[29] permits of deductions as to molecular symmetry. These authors discuss the application of their theory to a number of simple molecules. Of recent experimental work in this direction, reference may be made to the investigations of C. M. Lewis and W. V. Houston,[30] especially upon ammonia (supporting a flat pyramidal model) and methane (confirming the high symmetry). The amount of data on rotational Raman spectra is relatively small, since with most molecules the rotational structure is not resolved. Attention will therefore be confined to vibrational frequencies.

Now the vibrational frequencies of a molecule of known structure depend upon the masses of the oscillating atoms and the restoring forces called into action by the deformations of the molecule from its normal shape. The masses being known, observation of the frequencies in the Raman effect may therefore be expected to yield information as to the forces. In the very simple case of the diatomic molecule, where there is only one (axial) vibration frequency, the motion may be assumed to be simple harmonic and the frequency may be written as $\nu = \sqrt{f/\mu}/2\pi$, where μ is the reduced mass and f (the so-called force constant of the link)[31] is the restoring force per unit displacement. Hence, from the observed value of the one frequency, the one unknown f may be calculated. To the list of values of f for diatomic molecules[32] there has recently been added[17] the value ($1{\cdot}68 \times 10^5$ dynes per cm.) for the double mercurous ion $(Hg - Hg)^{++}$.

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[29] *Z. Physik*, 1933, **81**, 209; *A.*, 1933, 446.

[30] *Physical Rev.*, 1933, [ii], **44**, 903; *A.*, 1934, 129.

For a molecule of known structure containing more than two atoms, however, the number of unknown constants required to compute the nuclear vibrational frequencies is greater than the number of observables (*i.e.*, measurable frequencies), and so it is necessary to make simplifying assumptions as to the nature of the forces concerned. The chief alternative sets of assumptions which have been used[33] are the central-force system and the so-called valency-force system. In the former, an alteration of the distance between any two atoms in a molecule is assumed to bring into action a proportional restoring force directed along the line joining the two nuclei. In the latter, on the other hand, it is assumed that restoring forces of the kind just mentioned are only exerted between atoms which are actually linked together in the formula of the molecule as usually written, and there is also the further assumption (not made in the central-force system) that an alteration of the angle between two bonds of an atom calls into action a proportional force directed normally to the bonds so as to oppose the deformation. Neither of these systems is completely successful in accounting for observed results[5, 33a] —a state of affairs that is not surprising since both certainly involve too great a degree of simplification. On the whole, however, it would seem that the valency-force system, which corresponds more closely to accepted chemical views, is the more satisfactory.

Very important additional information as to the forces between atoms in molecules is to be expected from the study of the changes in vibrational frequency resulting from the replacement of an atom by one of its isotopes. Such a replacement leaves the forces practically unaltered, but the change of mass alters the frequencies and so increases the number of observables. A. Langseth [34] has shown that the isotopy of chlorine gives rise to a fine structure of one of the lines of chloroform, and an effect observed in the Raman spectrum of benzene has been ascribed [35] to the presence of C^{13}. Much bigger and more easily observable frequency changes are produced, however, by the substitution of hydrogen by its heavier isotope deuterium, and results of the utmost importance may be anticipated from the study of these effects. Already, the Raman spectrum of heavy water has been investigated both in the vapour [36] and in the liquid [37] state, and preliminary results are published for heavy acetylene C_2D_2 [38] and for a liquid which was thought to be heavy benzene C_6D_6.[39]

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[31] A. Dadieu and K. W. F. Kohlrausch, *Ber.*, 1930, **63**, [*B*], 251; *A.*, 1930, 663; cf. *Ann. Reports*, 1931, **28**, 371.

[32] *Ann. Reports*, 1931, **28**, 401, top of Table I.

[33] First introduced by N. Bjerrum, *Verhandl. deut. physikal. Ges.*, 1914, **16**, 737.

[33a] See, *e.g.*, the recent applications to paraffins, K. W. F. Kohlrausch and F. Köppl, *Z. physikal. Chem.*, 1934, [*B*], **26**, 209; *A.*, 942.

Quite generally, a fundamental vibrational frequency ν_i of a polyatomic molecule may be expressed in the same form as before, *viz.*, $\nu_i = \sqrt{f_i/\mu_i}/2\pi$, and may be regarded as involving the periodic variation of a certain so-called normal co-ordinate q_i (the analogue of the distance between the atoms in the diatomic case). The important points to note are that q_i involves the relative positions of all the atoms taking part, that f_i involves all the forces between them, and that μ_i involves all the masses. Hence, the frequency ν_i cannot, in general, be located in any particular part of the molecule, nor can f_i be ascribed to any particular link : the whole molecule vibrates. Now the interest of the chemist is directed primarily towards the force constants of particular links, and it would at first sight appear hopeless to deduce these from the observed frequencies of (say) a complicated organic molecule. In actual fact, however, examination of a large number of organic substances has brought to light many remarkable empirical simplifications. It appears that certain groups always give rise to their own characteristic Raman lines, the frequencies of which are more or less independent of the constitution of the rest of the molecule. We find in the Raman effect, as in other properties, that high degree of group individuality which is one of the main characteristics of organic chemistry.

Many of the empirical regularities have been discovered in the extensive investigations of K. W. F. Kohlrausch and his collaborators. A general account (up to 1931) is to be found in the book to which reference has already been made,[5] while later results are summarised in two interesting general articles[40] which K. W. F. Kohlrausch has recently published. To illustrate the kind of rule which is found to hold, we may take as example[41] the Raman spectrum of *iso*propyl mercaptan $(CH_3)_2CH{\cdot}SH$. This is made up approximately of (1) the characteristic lines (so-called inner group frequencies) of the respective groups SH, CH_3, and CH; and (2) lines ascribable to the assemblages $(CH_3){\cdot}CH{\cdot}(CH_3)$ and $(CH){\cdot}(SH)$, regarding (CH_3), (CH), and (SH) as individual "atoms" of masses 15, 13, and 33 respectively. The justification for this approximate way of regarding the molecule is based upon analysis and comparison of the frequencies of a large number of compounds of known structure. The inner group frequencies, as deduced by empirical inspection of the spectra of different substances, are not exactly constant. In the particular case of SH, however, the constancy is very good (variations of less than 0·3% for different mercaptans). It becomes permissible, therefore, to regard this group as an individual diatomic oscillator, and to work out an approximate force constant for the stretching of the link. In other cases (*e.g.*, C:O, see below), the constancy is not nearly so satisfactory: the remainder of the molecule exerts a much larger constitutive influence. Nevertheless, an interesting list of approximate force constants for organic links may be added to the list for diatomic molecules.[42] A notable result is obtained[43] by considering, instead of the force constant f, the mean restoring force K in the vibration. This is given by $K = \frac{1}{2}fa$, where a is the amplitude. It transpires that the K values for typical organic single, double, and triple links are approximately in the ratio 1 : 2 : 3.

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[34] *Z. Physik*, 1931, **72**, 350; *A.*, 1931, 1353.

[35] P. Grassmann and J. Weiler, *ibid.*, 1933, **86**, 321; *A.*, 1934, 10.

[36] D. H. Rank, K. D. Larsen, and E. R. Bordner, *J. Chem. Physics*, 1934, **2**, 464; *A.*, 1155.

[37] R. W. Wood, *Physical Rev.*, 1934, [ii], **45**, 392; *A.*, 583; *Nature*, 1933, **132**, 970; *A.*, 129; *ibid.*, 1934, **133**, 106; *A.*, 238.

[38] G. Glockler and H. M. Davis, *Physical Rev.*, 1934, **46**, 535.

[39] J. W. Murray, C. F. Squire, and D. H. Andrews, *J. Chem. Physics*, 1934, **2**, 715; *A.*, 1289.

A further approximate sub-division of vibrations[44] is into (1) so-called valency vibrations (ν-type), in which the main displacement is a stretching of valency links; and (2) bending or so-called deformation vibrations (δ-type), in which the main displacement is an alteration of valency angles. Thus, two of the three frequencies of $(CH_3){\cdot}(CH){\cdot}(CH_3)$, considered as a non-linear "triatomic" assemblage (see above), are of the ν-type, and the third is of the δ-type. The characteristic CH frequencies also fall into the same two classes.

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[40] *Naturwiss.*, 1934, **22**, 161, 181; *A.*, 472; *Z. Elektrochem.*, 1934, **40**, 429; *A.*, 942; see also M. Bourguel, *Bull. Soc. chim.*, 1933, [iv], **53**, 469; *A.*, 1933, 998.

[41] K. W. F. Kohlrausch, *Z. Elektrochem.*, 1934, **40**, 429; *A.*, 942.

[42] See *Ann. Reports*, 1931, **28**, 401, Table I.

[43] K. W. F. Kohlrausch, *op. cit.*, p. 162.

[44] R. Mecke, *Leipziger Vorträge*, 1931, p. 23; *Z. physikal. Chem.*, 1932, [*B*], **16**, 409; *A.*, 1932, 559; *ibid.*, [*B*], **17**, 1; *A.*, 1932, 675.

Considerations as to the approximate relative magnitudes of the force constants of stretching and bending make possible[44] an allocation of frequencies, not only to particular groups in a molecule, but also to ν- or δ-types.

The quantity k introduced by R. Mecke (*loc. cit.*) to characterise the "rigidity" of a linkage between two atoms differs from both the force constant f and the mean restoring force K mentioned above. Mecke's k, which shows remarkable regularities (*e.g.*, is practically constant for a series like the hydrogen halides), is defined as the work which would be expended in doubling the length of the link if Hooke's law were obeyed. Consequently, the expression for the frequency involves, in addition to k and the reduced mass μ, the distance r between the atoms concerned. To calculate k from an observed frequency, it is necessary to know r, as determined by some other method such as X-ray diffraction. Conversely, if the value of k be deduced from analogy to other similar compounds, then it is possible to calculate interatomic distances, etc., from observed frequencies. R. Titéica[45] has recently worked out molecular constants for a number of organic compounds by this approximate method, and has obtained results in fair agreement with those deduced by other methods.

As to the constitutive influence of the rest of the molecule upon a frequency characteristic of a given group, a few examples (selected from a great mass of data) must suffice to indicate the sort of regularity observed. K. W. F. Kohlrausch and F. Köppl[33] find that the unbranched paraffins from C_5H_{12} to $C_{12}H_{26}$ give a δ-type frequency which falls progressively with increase of chain length, and a ν-type frequency which oscillates in magnitude according as the number of carbons is odd or even. Another interesting empirical regularity is observed in the contribution of the group CX (X = Cl, Br, I) at the end of a hydrocarbon chain. It appears that this group can be associated in certain cases with a single Raman line, and in other cases with two lines close together. The doubling has been empirically related[46] to the possibility of "free rotation" round the bond, although no such relation is to be expected from theoretical considerations of a simplified model.[47] The recent interesting investigations of the freedom of rotation around a single bond by S. Mizushima, Y. Morino, and K. Higasi will be dealt with below in connexion with molecular symmetry. K. W. F. Kohlrausch and collaborators[48] have investigated the C:O frequency in a number of different compounds of the type X·CO·Y. If X is an alkyl group, then the C:O frequency is independent of the nature of the chain, except for small changes produced by alteration of the degree of branching at the α-carbon. The biggest variations of the C:O frequency (up to 9%) are produced by variation of the group Y attached directly to the C:O group. The important point which emerges is that the effects of the groups introduced depend, not simply upon their masses, but rather upon their polar characters.[49] Hence it follows that the observed frequency changes are primarily related to changes in the force constant of the C:O linkage, and not merely to changes in the reduced mass. Conjugation of the double bond of C:O with another double bond is found to cause an increase of intensity of the characteristic line.[50] Such knowledge of the behaviour of the C:O frequency, together with other similar empirical rules, makes it possible to use the Raman effect to investigate such questions as keto–enol tautomerism[51] and the structure of anhydrides.[52]

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[45] *Ann. Physique*, 1934, [xi], **1**, 533.

[46] K. W. F. Kohlrausch, *Z. physikal. Chem.*, 1932, [*B*], **18**, 61; *A.*, 1932, 897; *ibid.*, 1933, [*B*], **20**, 217; *A.*, 1933, 446; cf. W. D. Harkins and R. R. Haun, *J. Amer. Chem. Soc.*, 1932, **54**, 3920; *A.*, 1933, 7.

[47] E. Bartholomé and E. Teller, *Z. physikal. Chem.*, 1932, [*B*], **19**, 366; *A.*, 1933, 114.

Special interest attaches to the empirical regularities which are observed in the Raman spectra of benzene[35] and its derivatives.[53] The relationships between these and the regularities for aliphatic compounds of known structure have recently been discussed by

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[48] K. W. F. Kohlrausch and A. Pongratz, *Monatsh.*, 1934, **64**, 374; *A.*, 1290; H. C. Cheng, *Z. physikal. Chem.*, 1934, [*B*], **26**, 288; *A.*, 1056; *ibid.*, **24**, 293; *A.*, 346; K. W. F. Kohlrausch and F. Köppl, *ibid.*, p. 370; *A.*, 473; K. W. F. Kohlrausch and A. Pongratz, *ibid.*, 1933, [*B*], **22**, 359, 373; *A.*, 1933, 1228; K. W. F. Kohlrausch, F. Köppl, and A. Pongratz, *ibid.*, **21**, 242; *A.*, 1933, 661; cf. G. R. Paranje and K. S. Savanur, *Indian J. Physics*, 1934, **8**, 503; *A.*, 1155.

[49] In this connexion, cf. M. Bourguel, *Compt. rend.*, 1932, **194**, 1736; *A.*, 1932, 676.

[50] Cf. K. Matsuno and K. Han, *Bull. Chem. Soc. Japan*, 1934, **9**, 88; *A.*, 473.

[51] K. W. F. Kohlrausch, *Z. Elektrochem.*, 1934, **40**, 429; *A.*, 942; K. W. F. Kohlrausch, F. Köppl, and A. Pongratz, *Anal. Fis. Quím.*, 1933, **31**, 315; *A.*, 1933, 998; T. Hayashi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1933, **21**, 69; *A.*, 1933, 764.

[52] K. W. F. Kohlrausch, A. Pongratz, and R. Seka, *Ber.*, 1933, **66**, [*B*], 1; *A.*, 1933, 144.

[53] See, *e.g.*, K. W. F. Kohlrausch and A. Pongratz, *Monatsh.*, 1934, **64**, 361; K. W. F. Kohlrausch, *ibid.*, 1933, **63**, 427; *A.*, 1934, 346; A. Dadieu, K. W. F. Kohlrausch, and A. Pongratz, *ibid.*, 1932, **61**, 426; *A.*, 1933, 209; *ibid.*, **60**, 253; *A.*, 1932, 898; K. Matsuno and K. Han, *Bull. Chem. Soc. Japan*, 1934, **9**, 88; *A.*, 473; *ibid.*, 1933, 8, 333; *A.*, 1934, 130; N. G. Pai, *Nature*, 1933, **132**, 968; *A.*, 129; J. W. Murray and D. H. Andrews, *J. Chem. Physics*, 1934, **2**, 119; *A.*, 473; F. W. Crawford and J. R. Nielsen, *ibid.*, p. 567; *A.*, 1155.

K. W. F. Kohlrausch,[54] who finds that the evidence favours the Kekulé formula for benzene. The arguments all involve the interpretation of the Raman spectra of benzene derivatives in terms of characteristic group frequencies, constitutive regularities, etc., deduced empirically from aliphatic compounds. Though the justification of such an interpretation is perhaps doubtful, and though the arguments taken singly would be unconvincing, the accumulated empirical evidence is most suggestive. (Concerning the symmetry of the benzene ring, see below.)

Similar considerations have been applied to the rings of pyrrole,[55] thiophen, and furan [56] by G. B. Bonino and his co-workers, who consider the data to accord best with a type of centric formula; but from an examination of the Raman spectra of compounds known to have conjugated double bonds in a ring, R. Truchet and J. Chapron [57] conclude that the objection to the Kekulé formula is over-ruled, and K. Matsuno and K. Han [58] likewise infer that the furan ring contains double links. The effects of conjugation upon the frequency associated with the C:C linkage have also been investigated by T. Hayashi,[59] L. Piaux,[60] and others.

It is interesting to inquire into the reasons for the observed high degree of individuality of organic groups in respect to vibrational frequencies. Some idea of the sort of factor which may occasion such individuality can be obtained from simple considerations of the diatomic group X·Y in the molecule R·X·Y, where R represents all the rest of the molecule. If Y is of relatively very small mass (*e.g.*, a hydrogen atom), its vibration will disturb the more massive X very little. Consequently, the rest of the molecule which is linked to X will be, as it were, unaware of the vibration of Y; and conversely, the vibration of Y will be practically unaffected by the rest of the molecule. Alternatively, if the linkage between X and R is relatively very weak, the extent to which the mutual vibrations of X and Y influence R (and *vice versa*) will be very small. Passing to more complicated cases, reference may be made to the work of E. Bartholomé and E. Teller,[47] who, using a much simplified model, have been able to explain theoretically the individual behaviour of a group such as C·Cl at the end of a hydrocarbon chain.

[54] *Naturwiss.*, 1934, **22**, 184; *A.*, 472.

[55] G. B. Bonino, R. Manzoni-Ansidei, and P. Pratesi, *Z. physikal. Chem.*, 1934, [*B*], **25**, 348; *A.*, 830.

[56] G. B. Bonino and R. Manzoni-Ansidei, *ibid.*, p. 327; *A.*, 830; see also G. Glockler and B. Wiener, *J. Chem. Physics*, 1934, **2**, 47.

[57] *Compt. rend.*, 1934, **198**, 1934; *A.*, 830.

[58] *Bull. Chem. Soc. Japan*, 1934, **9**, 327; *A.*, 1155.

[59] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **23**, 274; *A.*, 473.

[60] *Compt. rend.*, 1934, **199**, 66; *A.*, 942.

Raman Effect and Molecular Symmetry.—In the applications outlined above, the Raman effect is considered merely as providing frequency values. The full information inherent in it cannot, however, be utilised without taking into account the other properties of the spectrum, such as number of lines, their relative intensities, states of polarisation, etc. A. Smekal's extreme quantum explanation [28] is not concerned with the mechanism of the effect, and so tells us nothing of these properties.

Now, although the effect was not observed experimentally until 1928,[4] the complete theory of the mechanism of the interaction of the light and the scattering system had already been worked out in 1925 by H. K. Kramers and W. Heisenberg,[61] using the correspondence principle; in 1926 by E. Schrödinger,[62] using wave mechanics; and in 1927 by P. A. M. Dirac,[63] using general quantum mechanics. These theoretical treatments all agree in giving the same final formula, from which all the properties of the scattered light may in principle be deduced. Unfortunately, the formula involves a summation, for which it is necessary to know all the energy levels of the scattering system in question, as well as all the probabilities of transitions between them. In very simple cases (diatomic molecules) the laborious summation can be carried out; [64] but the requisite data are in general lacking, so that the result (though of extreme theoretical interest) is at present of no practical value for the purpose of interpreting Raman spectra.

Undoubtedly the greatest advance in this connexion, and one which has given a considerable impetus to experimental work, is G. Placzek's polarisability theory.[65] This author has recently published a complete account of the mathematical-physical treatments of the Raman effect of free molecules,[66] to which reference may be made for all details. A less thorough, but perhaps more easily readable account, is to be found in a lecture by J. Cabannes.[67] In his polarisability theory, G. Placzek starts out from the consideration that, although the Raman frequencies are nuclear frequencies, yet the actual scattering of the light must be due practically entirely to the less massive electrons. Attention must therefore be directed to the interaction between nuclear vibrations and the surrounding "electron atmosphere." In the first place, light scattering without change of frequency (classical or Rayleigh scattering) may be visualised as due to the periodic polarisation of the electron atmosphere by the oscillating electric field of the incident light waves, *i.e.*, the production of an induced electric dipole moment oscillating with the incident frequency ν_0. The property of the molecule governing this effect is its polarisability α, which is representable by a sphere when the molecule is optically isotropic and by an ellipsoid when it is optically anisotropic. The shape of this ellipsoid determines, in particular, the state of polarisation of the Rayleigh line, as measured by a suitably defined and experimentally accessible degree of depolarisation ρ. A nuclear vibration of frequency ν causes, in general, a corresponding periodic alteration of the polarisability α; the ellipsoid is now no longer constant, but altering (in shape, orientation, etc.) at frequency ν. As far as the oscillating electric moment induced by the incident light is concerned, this superimposes upon the periodicity ν_0 a new periodicity ν, and the two together give the frequencies $\nu_0 \pm \nu$. These therefore appear in the scattered spectrum, *i.e.*, we have the Raman effect.

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[61] *Z. Physik*, 1925, **31**, 681.

[62] *Ann. Physik*, 1926, [vi], **81**, 109.

[63] *Proc. Roy. Soc.*, 1927, [*A*], **114**, 710.

[64] J. H. van Fleck, *Proc. Nat. Acad. Sci.*, 1929, **15**, 754; C. Manneback, *Z. Physik*, 1930, **62**, 224; *A.*, 1930, 840.

[65] *Z. Physik*, 1931, **70**, 84; *A.*, 1931, 893; *Leipziger Vorträge*, 1931, 71.

[66] "Handbuch der Radiologie," Vol. 6, Part 2, p. 205, Akademische Verlagsges., Leipzig, 1934.

[67] "La Structure des Molécules et la Diffusion de la Lumière," Bermejo, Madrid, 1932 (in French).

It follows that, just as the Rayleigh line is characterised by the quantity α, so is a Raman line characterised by the alteration of α caused by the respective nuclear vibration, *i.e.*, by the quantity $(\partial\alpha/\partial q)_0$, where q is the normal co-ordinate of the vibration, and the suffix zero denotes that the value of $\partial\alpha/\partial q$ is to be taken at the equilibrium position of the nuclei. The general selection rule for Raman lines becomes at once obvious: if a nuclear vibration is such that it leaves α unaffected or causes it to pass through a maximum or minimum as the nuclei pass through their mean positions, then $(\partial\alpha/\partial q)_0 = 0$, and the corresponding line is forbidden in the Raman effect. Of course, these considerations tell us nothing about whether the frequency in question is forbidden or permitted in direct infra-red absorption or emission, which are subject to quite different selection principles.

The intensity of a Raman line will be greatest when $(\partial\alpha/\partial q)_0$ is greatest, *i.e.*, when the nuclear vibration most affects the "electron atmosphere." In the case where only one linkage is involved, it follows that the intensity will decrease with decrease in the degree of electron sharing (*i.e.*, with decrease in the homopolar character of the link) and will finally vanish when the binding becomes completely polar (*i.e.*, when the "electron atmospheres" of the atoms—now ions—become independent). This is precisely the conclusion reached empirically by P. Krishnamurti[68] from systematic investigations of inorganic chlorides. Intensity measurements have been used by I. Hansen-Damaschun [69] as a criterion of the degree of homopolarity of linkages in inorganic complexes. R. Samuel and M. J. Khan [70] have also observed a quite different effect, *viz.*, that the magnitude of the CN frequency in complex cyanides appears to increase with increase of homopolarity.

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[68] *Nature*, 1930, **125**, 892; *A.*, 1930, 978; *Indian J. Physics*, 1930, **5**, 113; *A.*, 1930, 1344; cf. *ibid.*, p. 633; A., 1931, 146.

The practical value of the polarisability theory as a source of information upon molecular structure might, at first sight, appear to be small in view of the fact (see above) that it is not, in general, possible to calculate nuclear frequencies without introducing doubtful simplifying assumptions as to the force systems. Actually, however, the theory goes on to make a number of fundamental deductions about the relation of Raman spectra to molecular structure by arguments quite independent of the special nature of the forces involved. These deductions, which are of great practical importance, are based upon pure symmetry considerations.

In the first place the total number $(3n - 6)$ of fundamental vibrational frequencies possessed by a molecule is determined simply by the number n of atoms it contains; and the number of these frequencies which have identical values (the degeneracy) is determined by the symmetry of the molecule considered as an assemblage of mass-points. Further than this, the molecular symmetry determines the symmetry properties of the different modes of vibration, and these clearly decide the quality of the corresponding variations of the polarisability α. But it is upon this quality that the properties (*e.g.*, states of polarisation) of the corresponding Raman lines depend. Hence, for a molecule containing a known number of atoms, the structural symmetry determines both the number N and the states of polarisation (ρ-values) of the Raman lines. Observation of N and the ρ-values therefore provides a powerful method of discriminating between different possible molecular symmetries. Considerations of space preclude any account here of the various rules of selection and polarisation, for details of which reference may be made to G. Placzek's treatise.[66] The practical application of the rules is facilitated by the complete tables which are given there. The example of a triatomic molecule XY_2 may serve to indicate the sort of deductions which the theory makes possible. If the molecule gives only one Raman line, the intensity being high and ρ being $< \frac{6}{7}$, then the molecule must be symmetrical and linear, *viz.*, $Y - X - Y$. A symmetrical but bent molecule (*i.e.*, the angle between the two bonds of the central X atom not equal to 180°) would give three Raman lines, of which two would have $\rho < \frac{6}{7}$ and the third $\rho = \frac{6}{7}$. An example of a molecule for which the Raman effect data indicate this bent type is sulphur dioxide. In his treatise, G. Placzek summarises the results of the application of his theory to the above types, as well as to molecules of the formula XY_3 (pyramidal or plane), XY_4 (tetrahedral), X_2Y_2 (acetylene, linear), XY_3Z (three-fold axis), etc. The conclusions are always in agreement with those afforded by other lines of inquiry.

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[69] *Z. physikal. Chem.*, 1933, [*B*], **22**, 97; *A.*, 1933, 886.

[70] *Z. Physik*, 1933, **84**, 87; *A.*, 1933, 886.

A notable complication may sometimes occur in connexion with the number of Raman lines which appear. The best example is carbon dioxide. This is known from other data to be a symmetrical linear molecule, and hence would be expected to give only one Raman line (see above). Actually, however, the spectrum is found [71] to consist chiefly of two strong lines rather close together. The explanation of this apparent anomaly was given by E. Fermi,[72] who showed that the doubling is due to a fortuitous commensurability between two of the fundamental vibration frequencies of the molecule, one of which chances to be almost exactly twice the other. In drawing deductions from the number of lines appearing in the Raman spectrum of a molecule, it is necessary to bear in mind the possibility of such a fortuitous increase, as well as the risk that a line, though permitted, may be so weak as to have escaped observation.

Measurements of the degree of depolarisation ρ serve to support and extend conclusions based on numbers of lines. Unfortunately, the experimental technique of accurate polarisation measurements [73] is incomparably more difficult than that of mere frequency determinations. However, data have been accumulated for a fairly large number of compounds, thanks to such workers as S. Bhagavantam,[74] J. Cabannes and A. Rousset,[73] P. Grassmann,[75] L. Simons,[76] B. Trumpy,[77] S. Venkateswaran,[78] and others. An interesting suggestion for the simplification of the technique of polarisation measurements, originally put forward by G. Placzek and W. R. van Wijk,[79] has been applied by L. S. Ornstein and P. Stoutenbeek.[80] The reversal or non-reversal of the direction of polarisation when the incident light is circularly polarised [81] is also explained by the polarisability theory,[66] and measurements of this effect can be used as additional evidence of molecular symmetry.

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[71] A. Langseth and J. R. Nielsen, *Z. physikal. Chem.*, 1932, [*B*], **19**, 35; *A.*, 1932, 1188; I. Hansen, *Physical Rev.*, 1934, [ii], **46**, 122; *A.*, 1056; see also A. Langseth, J. U. Sörensen, and J. R. Nielsen, *J. Chem. Physics*, 1934, **2**, 402; *A.*, 942.

[72] *Z. Physik*, 1931, **71**, 250; *A.*, 1931, 1111; see also D. M. Dennison, *Physical Rev.*, 1932, [ii], **41**, 304; *A.*, 1932, 982; A. B. D. Cassie and C. R. Bailey, *Z. Physik*, 1932, **79**, 35; *A.*, 1933, 6; G. P. Ittmann, *Physica*, 1933, **13**, 177.

[73] See, *e.g.*, J. Cabannes and A. Rousset, *Ann. Physique*, 1933, [x], **19**, 229; *A.*, 1933, 446.

[74] *Indian J. Physics*, 1932, **7**, 79; *A.*, 1932, 793.

[75] *Z. Physik*, 1932, **77**, 616; *A.*, 1932, 1075.

[76] *Comm. Phys.-math. Soc. Sci. Fennica*, 1932, **6**, No. 13, 1.

[77] *Z. Physik*, 1934, **88**, 226; *A.*, 583; *ibid.*, 1934, **90**, 133; *A.*, 1056.

[78] *Phil. Mag.*, 1933, [vii], **15**, 263; *A.*, 1933, 337.

Amongst recent work, mention may be made of investigations upon the hexafluorides of sulphur [82] and other elements,[83] which support an octahedral model. This is in harmony [84] with the conclusions from earlier work [85] upon other systems of the type XY_6. D. M. Yost and J. E. Sherborne [86] have recently obtained the Raman spectrum of arsenic trifluoride, for which the selection rules indicate a pyramidal structure. The polarisation measurements of A. Langseth, J. R. Nielsen, and J. U. Sörensen [87] upon the azide and the thiocyanate ion give evidence for a linear structure in both cases, the former being centrally symmetrical. Of special interest is the evidence obtainable as to the symmetry of the benzene ring. Perhaps the most remarkable fact in this connexion, pointed out by G. Placzek,[88] is that the experimental data for liquid benzene are incompatible with the presence of a centre of symmetry. The whole question of the benzene ring has recently been considered by J. Weiler,[89] who concludes that the data provide support for a three-fold symmetry (such as would be given by the Kekulé formula) rather than for a six-fold symmetry (such as must result if the ring is plane and all the carbons are equivalent). Reference has already been made to the work upon heterocyclic rings,[55, 56] which also involved some symmetry considerations.

An interesting deduction concerning simple *cis-* and *trans-*

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[79] *Z. Physik*, 1931, **67**, 582; *A.*, 1931, 408.

[80] *Ibid.*, 1933, **85**, 754; *A.*, 1933, 1228.

[81] W. Hanle, *Physikal. Z.*, 1931, **32**, 556; *A.*, 1931, 997; *Ann. Physik*, 1931, [v], **11**, 885; *A.*, 1932, 108; *ibid.*, 1932, [v], **15**, 345; *A.*, 1933, 114; R. Bär, *Helv. Physica Acta*, 1931, **4**, 130; P. Daure, *Compt. rend.*, 1934, **198**, 725; *A.*, 346.

[82] A. Eucken, H. Ahrens, E. Bartholomé, and L. Bewilogua, *Z. physikal. Chem.*, 1934, [*B*], **26**, 297; *A.*, 1055.

[83] D. M. Yost, C. C. Steffens, and S. T. Gross, *J. Chem. Physics*, 1934, **2**, 311; *A.*, 830.

[84] O. Redlich, T. Kurz, and P. Rosenfeld, *ibid.*, p. 619; *A.*, 1155.

[85] *Idem*, *Z. physikal. Chem.*, 1932, [*B*], **19**, 231; *A.*, 1933, 113.

[86] *J. Chem. Physics*, 1934, **2**, 125; *A.*, 473.

[87] *Z. physikal. Chem.*, 1934, [*B*], **27**, 106.

[88] Ref. (66), p. 334.

[89] *Z. Physik*, 1934, **89**, 58; *A.*, 716; but cf. E. B. Wilson, *Physical Rev.*, 1934, [ii], **46**, 146.

isomerides can be drawn [66] from the symmetry theory, *viz.*, that the centre of symmetry of the *trans*-form must result in fewer Raman lines for this isomeride than for the *cis*-form. This is borne out by experiment.[90] B. Trumpy [77] has also measured the polarisations of the lines of the *cis*- and *trans*-isomerides of dichloro- and dibromo-ethylene and found them to agree with the theory.

Similar symmetry considerations underlie the recent investigations of S. Mizushima, Y. Morino, and K. Higasi [91] upon the freedom of rotation around the C–C link in *s*-dichloroethane. Starting from the idea that alteration of the relative positions of the two chlorines by rotation, though considerably altering the intensities of certain Raman lines, may not appreciably affect their frequencies, these workers have made measurements of the ratio of the intensities of two of the Raman lines of this compound in various solvents. They find that the ratio shows a regular variation with the dielectric constant of the solvent. Actually, the observed differences are not large, and further confirmation of the effect is desirable. The result, which is brought into relation with similar regularities in the observed dipole moment, is explained by the authors as due to the different relative times spent by the molecule in configurations approximating to those in which the chlorines are in the *cis*- and the *trans*-position respectively. L. A. W.

3. THE THEORY OF RESONANCE AND THE CO-ORDINATION OF HYDROGEN.

The theory of resonance in structural chemistry has already been discussed in these Reports.[1] Recent work has established it on a firmer basis, and it must now be taken seriously into account by organic as well as by physical chemists. Only a brief summary will be given here, sufficient to make it possible to understand its application to the co-ordination of hydrogen.

It can be shown that if two electronic structures are possible for the same molecule, the wave-mechanical function for the normal state of the molecule is not either of those expressing the two separate states, but a linear combination of the two. This means that the molecule in question must be regarded either as passing from one state to the other with very great frequency (some 10^{15} times per second), or more probably as having a structure intermediate between the two, which cannot be expressed by the symbols of structural chemistry. The conditions for such resonance to be possible are (1) that the two structures do not differ greatly in energy, and (2) that the atoms occupy practically the same positions in both; the change, if there is one, is far too rapid for the atoms, even hydrogen atoms, to move with it. As a result of this resonance the molecule will show the properties of both structures, but in different degrees, the form with the larger energy content (smaller stability) having the less influence. Two further consequences of importance for detecting the occurrence of the phenomenon are (1) that the heat of formation of the molecule, and hence also its stability, is greater than that of either structure, and (2) that the distances between the linked atoms are somewhat smaller. The conception of resonance is originally due to Hund, but its application to molecules has been largely the work of Pauling and his school; some of the more important references are given.[2–9]

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[90] A. Dadieu, A. Pongratz, and K. W. F. Kohlrausch, *Monatsh.*, 1932, **60**, 205, 221; *A.*, 1932, 898.

[91] *Physikal. Z.*, 1934, **35**, 905.

[1] C. N. Hinshelwood, *Ann. Reports*, 1932, **29**, 17; 1933, **30**, 44.

As an example we may take carbon dioxide. There are three possible structures, the last two being identical:

	$O=C=O$	$O\leftarrow C\overset{\leftarrow}{\equiv}O$	$O\overset{\rightarrow}{\equiv}C\rightarrow O$	Obs.
Distance, Å.U.	$\underbrace{1\cdot28\quad1\cdot28}_{2\cdot56}$	$\underbrace{1\cdot43\quad1\cdot13}_{2\cdot56}$	$\underbrace{1\cdot13\quad1\cdot43}_{2\cdot56}$	2·30
Heat of formation from atoms, kg.-cals.	348	*ca.* 350	*ca.* 350	380

If we may assume that the length and the heat of formation of a co-ordinate link are the same as those of a normal covalency (which is probable, though the evidence is not so strong as could be wished), the heats of formation of the three forms are nearly the same; they are all linear molecules, and the distances vary only to the small extent caused by the change in the multiplicity of the link. Thus the essential conditions of resonance are satisfied, and we should expect it to occur. If it does so, the heat of formation of carbon dioxide should be greater, and the lengths of the links less, than corresponds to the structure $O=C=O$. The values to be expected for the three forms are given beneath the formulæ; the observed

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[2] L. Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 3225 (one-electron links).

[3] *Idem, ibid.*, 1932, **54**, 988, 3570 (resonance of covalent and electrovalent links).

[4] *Idem, Proc. Nat. Acad. Sci.*, 1932, **18**, 293, 498 (interatomic distances).

[5] L. Pauling and D. M. Yost, *ibid.*, p. 414; L. Pauling and J. Sherman, *J. Chem. Physics*, 1933, **1**, 606 (heats of formation).

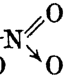
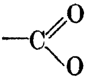
[6] L. Pauling and G. W. Wheland, *ibid.*, p. 362; L. Pauling and J. Sherman, *ibid.*, p. 679 (application to aromatic and hydroaromatic compounds).

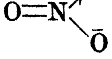
[7] G. W. Wheland, *ibid.*, p. 731 (keto-enols).

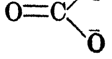
[8] L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, 1933, **19**, 860; N. V. Sidgwick, *Trans. Faraday Soc.*, 1934, **30**, 801 (organic azides).

[9] L. E. Sutton, *ibid.*, p. 789 (dipole moments and resonance).

C–O distance is 1·15 Å.U. instead of the 1·28 required for C=O,[4] and the heat of formation is 32 kg.-cals. greater than that calculated from the value for a carbonyl group in aldehydes and ketones.[5] In the papers quoted above, many other examples are given, in which the resonance is indicated by the heats of formation or the interatomic distances, or in some [4, 8, 9] by the electrical dipole moments. This last criterion is of peculiar interest, because it enables us to distinguish between resonance and tautomerism in its ordinary sense. In many molecules, as in nitrous oxide and the organic azides, the two structures have considerable but oppositely directed moments, and the observed moment is very small. The opposing moments of the two forms can only neutralise one another if their time of change is less than that required for the turning of the polar molecule in the electric field, which is of the order of 10^{-12} second.[10] In resonance, where the time of change (if we consider a change as occurring) is of the order of 10^{-15} second,[9] this condition is fulfilled. But a mixture of the two forms in chemical equilibrium (a tautomeric mixture) would change much more slowly, and must have a moment which is a weighted arithmetic mean of the separate moments, since the direction (with respect to the molecule) will not affect the polarisation, which depends on the square of the moment.

Familiar examples of resonance are afforded by the symmetry of the  group (indicated by the dipole moments), of the  ion, and of the NO_3' and CO_3'' ions. The crystallographic evidence shows that the last two are plane structures, as is required by the tetrahedral theory for the formulæ (I) and (II), but further,

(I.) 

 (II.)

that the three oxygen atoms are at the points of an equilateral triangle, with the nitrogen or carbon at the centre. This implies a resonance, with the double link not localised on any particular oxygen atom. Here, too, we find the characteristic shortening of the link. The values are: for NO_3', N–O 1·36, N=O 1·22 (mean 1·31), obs. 1·23; for CO_3'', C–O 1·43, C=O 1·28 (mean 1·38), obs. 1·23 Å.U.[11] A further example is the "oscillation" of the ionic charge in the ions of the triphenylmethane and the cyanine dyes, which seems to be the cause of their intense colours.

[10] P. Debye, *Trans. Faraday Soc.*, 1934, **30**, 679.

[11] V. M. Goldschmidt, Freudenberg's "Stereochemie," 1933, p. 50.

The resonance theory of structure, if, as seems probable, it is to be accepted, is a most important advance in the theory of structural chemistry. It shows that the behaviour of a compound can often not be expressed by a single formula, but only by the combination of two, and this, not in the tautomeric sense that the substance is a mixture of two kinds of molecule, but in the sense that every molecule has, at least to some extent, all the properties represented by the two structures, as well as other properties which are directly due to the resonance, especially an increase of stability, which ensures that the resonance will always occur when it is possible. It is to be presumed that the modern organic theories which ascribe the reactivities of molecules to drifts of their linking electrons, are to be interpreted with reference to the theory of resonance.

Co-ordination of Hydrogen.

As was pointed out in last year's Report,[12] the evidence accumulated in recent years has strengthened our belief in the occurrence of this co-ordination—in the power of the hydrogen atom to hold two other atoms together—but it has also shown that the original suggestion, that such a hydrogen atom has four shared electrons, is untenable. The solution of the difficulty is provided by the theory of resonance, the hydrogen being covalently attached to one and the other of the two atoms in the two structures. This implies that the distance between the two atoms linked by the hydrogen is shorter than in either of the separate structures, which is found to be the case. In solid sodium hydrogen carbonate, for example, the shortest distance between two oxygen atoms of different CO_3 groups, where there is no linking hydrogen, is 3·15 Å.U.; the insertion of a hydrogen atom to form $O{-}H\ O$, if there were no resonance, should at least not shorten this, whereas the observed distance between the oxygen atoms in $O{-}H \cdot \cdot O$ is only 2·55 Å.U.[13] The heats of formation of the two forms would not be expected to differ greatly, since they only involve a rearrangement of the bonds between the same atoms; the extra energy caused by the resonance is shown by the stability of the co-ordinated form. The conditions of resonance are therefore present, and we have to consider what the various resonating structures are. They may be divided into two classes, (I) those in which resonance can occur without ionisation, which implies that the co-ordinated structure is cyclic, and (II) those in which ionisation is involved.

(I). If the hydrogen atom can be linked without ionisation to either of the two atoms that it holds together (which for simplicity we may suppose to be oxygen), these two atoms must be part of the same molecule, and a rearrangement of links must take place along the chain, which will be joined through the hydrogen to form a chelate ring. The process may involve one molecule (I*a*) or two (I*b*).

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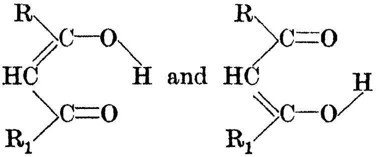
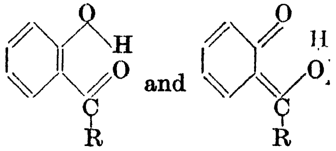
[12] *Ann. Reports*, 1933, **30**, 112.

[13] W. H. Zachariasen, *J. Chem. Physics*, 1933, **1**, 634.

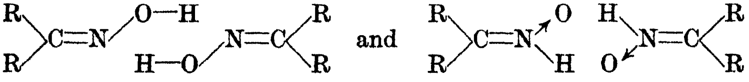
(I*a*). It occurs within one molecule in the ordinary chelation through hydrogen, as in the keto–enols or the *o*-aldehydophenols :





The strain in a 6-ring with two double links is very small, and hence the same position of the atoms fits either structure. This mechanism explains the symmetry of the ring, and the fact that two isomeric enols of this type have never been isolated. In the *o*-phenol derivatives the second form is *o*-quinonoid ; if we assume that in the benzenoid form the chelate 6-ring fixes the double link between the atoms common to both rings,[14] it will be seen that the other two double links in the aromatic ring have the same positions in both structures, which is supported by the recent results of W. Baker.[15] We can also see why the tendency to chelation practically disappears when the β-keto-enols are reduced to β-keto-alcohols, $R\cdot CH(OH)\cdot CH_2\cdot CO\cdot R_1$, since the migration of the double link from one oxygen to the other is no longer possible, and a co-ordination of the hydrogen can only occur as it does in the alcohols (see II, below) where the resonance energy is much weaker.

(I*b*). Sometimes this ring-formation can occur only by the combination of two molecules. This is what happens with carboxylic acids [16] and with oximes. Both these classes readily polymerise to double molecules but no further, the co-ordinating power being thereby exhausted. In the oximes, the second form must have the imino-structure, from which the *N*-ethers are derived :



(II). To explain the association of simple hydroxylic compounds, such as water, alcohols, and phenols, where the co-ordination of the hydrogen will give chains and not rings, some other mechanism must be found. It is well known that, in high dilution, molecules of this kind are less polymerised than carboxylic acids or oximes, but that with rising concentration the polymerisation increases indefinitely, and can go far beyond the dimeric stage.[17] This must occur through the formation of oxonium ions :

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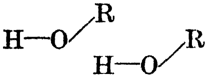
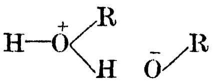
[14] W. H. Mills and I. G. Nixon, *J.*, 1930, 2510.

[15] *J.*, 1934, 1684.

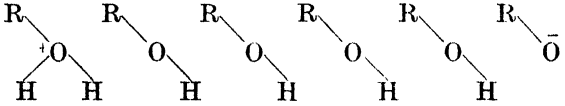
[16] *Ann. Reports*, 1933, **30**, 115.



and



The simple molecules will be held in the positions required for the oxonium formation by the energy of the resonance. It is clear that this process can be extended indefinitely through a series of molecules, giving as the ionised form :



(For simplicity the atoms are here arranged on the plane model; actually, of course, the steric relations will be more complicated.) So long as the addition of another ROH molecule causes an increased evolution of energy, the chain will be able to lengthen, but the tendency of the thermal agitation will be to break it up, and an equilibrium will be reached in which the degree of association will be greater the lower the temperature. It will be seen that, in a chain of this kind, all the ROH molecules other than those at the ends are in the same state as a free ROH, except that their relative positions are determined by the resonance, and presumably they are brought nearer together than if the resonance did not occur. This gives us a picture of the state of hydroxylic liquids very like the "pseudo-crystalline" state suggested for liquid water by J. D. Bernal and R. H. Fowler; [18] it is obvious that in water itself there are further possibilities of resonance which do not occur when one of the hydrogen atoms is replaced by an alkyl radical. The theory explains many of the properties of water and hydroxylic compounds in general. It will be seen that the $RH_2O^{\cdot}$ and OR' ions are not free so long as the resonance persists; the whole chain forms a "zwitterion," and cannot contribute to the conductivity; this will be due only to those ions which are displaced from the chain by the thermal agitation. Thus the minute conductivity of pure water is quite in accordance with the theory, which also explains why the number of free ions grows larger as the temperature, and hence the kinetic energy of the molecules, increases.

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[17] See, *e.g.*, F. S. Brown and C. R. Bury, *J. Physical Chem.*, 1926, **30**, 694; *A.*, 1926, 675.

[18] *J. Chem. Physics*, 1933, **1**, 515; *A.*, 1934, 13; *Trans. Faraday Soc.*, 1933, **29**, 1049; *A.*, 1933, 1106.

The structure of the chains makes it possible, as Bernal and Fowler have pointed out, to account for the abnormal mobility of hydrogen and hydroxyl ions. As the temperature rises, the chains will on the average become shorter, and this abnormality should diminish, as in fact it does: the mobility of the hydrogen ion is six times as great as that of the potassium ion at 0°, but only four times as great at 50°.

Co-ordination of hydrogen with atoms other than oxygen, as in $[\mathrm{F{-}H{\leftarrow}F}]'$ and in undissociated $\mathrm{R_3NH{\leftarrow}OH}$, can obviously be explained in the same way.

If this theory is adopted, it clearly gives quite a different mechanism for the co-ordination of hydrogen from that generally accepted for the co-ordination of other atoms, such as those of the metals in the β-diketone derivatives. The reason why the same compounds, such as the β-keto-enols, give rise to both classes of derivatives is that the shape of the molecule allows of the formation of a nearly strainless ring. The difference in the mechanism of the linkage may explain why certain molecules, such as ethylenediamine and glycollic acid, form chelate rings through metallic atoms, but not through hydrogen. The remarkable and regular variation in the power of a hydrogen atom to co-ordinate, according to the atom with which it is united ($\mathrm{H{-}F} > \mathrm{H{-}O} > \mathrm{H{-}N} > \mathrm{H{-}C}$; $\mathrm{H{-}F} > \mathrm{H{-}Cl}$; $\mathrm{H{-}O} > \mathrm{H{-}S}$), must be due, in part at least, to a difference in the readiness with which the resonance occurs, *i.e.*, in the stability of the second (ionised) form. The view that the co-ordination of hydrogen is due to a different mechanism from that of a metal is supported by the work on absorption spectra by R. A. Morton, A. Hassan, and T. C. Calloway,[19] who conclude that "chelation through hydrogen of the mono-enol [of a β-diketone or β-keto-ester], if it occurs at all, must be different in kind from the chelation which obtains with metallic derivatives." N. V. S.

4. HEATS OF FORMATION IN HOMOLOGOUS SERIES.

F. D. Rossini [1] has recently determined the heats of combustion of the lower normal paraffins and primary alcohols with an accuracy greater than that hitherto attained, the errors (per g.-mol.) not exceeding 150 cals. per carbon atom. The results are surprising, and of great interest.

If *Q* is the heat of combustion per g.-mol. of a substance, and *P* that of its carbon and hydrogen (and other elements, if any), these being taken as graphite, hydrogen gas, etc., then H_f, the heat of formation of the compound from these elements, is equal to $P - Q$. If we further know the heat $H_{at.}$ required to convert these quantities of graphite, hydrogen gas, etc., into their atoms, then the heat of formation of 1 g.-mol. of the compound from its component atoms $H_a = H_{at.} + P - Q$; H_a is the total energy evolved in the formation of all the links in the molecule, and obviously this energy, or the stability of the molecule, will be greater the smaller the heat of combustion Q.

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[19] *J.*, 1934, 900.

[1] *Bur. Stand. J. Res.*, 1934, **12**, 735; **13**, 21, 189.

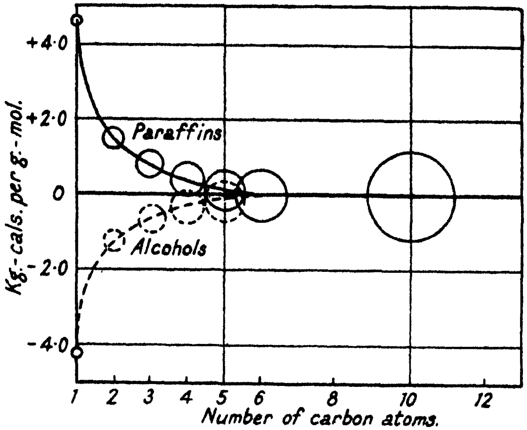
It was previously supposed that the heats of combustion (and hence also the heats of formation) of the paraffins showed a constant increase per CH_2 from methane upwards; this implied that the heat of formation was strictly additive for the links, being of the form $xA + yB$, where x and y are the numbers in the molecule, and A and B the heats of formation, of the C–C and the C–H links respectively. Rossini has shown that this is true when n, the number of carbon atoms, is greater than 5, but that as we descend the series below this, the heat of formation becomes increasingly greater than would be expected, the value for methane showing an excess of 4·8 kg.-cals. With the alcohols, he finds the opposite effect: where n is more than 5, the additive rule again holds, with the same increment per methylene group as in the paraffins, but in the lower homologues the heat of formation becomes increasingly less, and that of methyl alcohol is 4·2 kg.-cals. smaller than the rule requires. Since the heats of combustion are far more accurately known than the heats of atomisation of the elements, the values quoted below are the observed departures of the heats of formation H_a from those calculated on the additivity rule; these are independent of the heats of atomisation assumed for the elements. The measurements are made at 25°, and are calculated for the compounds in the gaseous state. Rossini has also calculated, by means of the specific heats, the departures at the absolute zero. These results are given in the table, the experimental error being added for the first series: it is much the same in the others.

Differences (obs. — calc.) in heats of formation for the gaseous state, in kg.-cals. per g.-mol.

No. of C atoms.	Paraffins.		Alcohols.	
	25° C.	0° K.	25° C.	0° K.
1	+ 4·61 ± 0·1	+ 4·81	— 4·18	— 3·78
2	+ 1·59 ± 0·2	+ 1·59	— 1·18	— 1·18
3	+ 0·83 ± 0·3	+ 0·84	— 0·60	— 0·60
4	+ 0·46 ± 0·4	+ 0·47	— 0·30	— 0·30
5	+ 0·13 ± 0·5	+ 0·15	— 0·15	— 0·15
6	0 ± 0·7	0	0	0
10	0 ± 1·2	0	0 ± 1·3	0
15	0 ± 1·8	0	—	—

The values at 25° are plotted against n in the fig.; the radii of the small circles indicate the probable errors.

These results account for a difficulty which has long been evident in the heats of formation of homologous series, that the increment per methylene group appears to be smaller in the paraffins than in any of their substitution products. The difference is not large, being about 2 kg.-cals. per CH_2, and so of the same order as the usual experimental error; but its existence seemed certain. It was, of course, obtained on the assumption that an additivity rule held in each series, and was mainly derived from the values for the lower members, where the experimental errors are smaller. It is obvious from Rossini's figures that for the lower members the increase per methylene group is less in the paraffins and more in the alcohols than the common value for the higher members of both series. Since it was previously found that, whatever X may be in $C_nH_{2n+1}X$, the increment is practically always greater than in the paraffins, we may expect that any other series of alkyl derivatives when examined with the same care will be found to give a curve of the alcohol type.



Various causes which might lead to this peculiarity of the paraffins had been discussed before,[2] and it was concluded that only two are possible. One is that it is due to differences in the rotational energy, the heats being referred to the ordinary temperature instead of the absolute zero, though it is improbable that this could account for so large a difference. This suggestion has been definitely disproved by Rossini's calculation of the values at the absolute zero, since the abnormalities are practically the same there as at

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[2] N. V. Sidgwick, "The Covalent Link," 1933, p. 116.

25°. The other possible explanation, which seems the only one left, is that the symmetry of the methane molecule causes an additional stability, and that this is interfered with when a C–H link is replaced by a C–CH_3, but more seriously when it is replaced by a C–O–H; so that we get an initial excess in the heat of formation in the first case and an initial defect in the second, both of which gradually disappear to give a common value as the molecule becomes predominantly composed of methylene groups. A quantitative physical explanation of this effect of symmetry is much to be desired.

These effects are, of course, small—the absolute value of the heat of formation of a C–H link is about 92 kg.-cals., while the difference per C–H in methane is 1·2 kg.-cals., or less than 1·5%—but they are large enough to make the calculation of the heats of other links very uncertain when we only know the heats of combustion of the lower members of a series, and these, as Rossini's results have shown, are not very accurate. For instance, if we try to find H_a for C–O–H by subtracting the value for C_nH_{2n+2} from that for $C_nH_{2n+1}OH$, the difference where $n = 1$ will be 8·8, and where $n = 2$, 2·8 kg.-cals., larger than in the higher members of the series. Rossini's work shows that no exact calculations of the heats of linkage can be made until the heats of combustion in general have been redetermined with greater accuracy.

In this connexion it should be noticed that recent determinations of the heats of atomisation of nitrogen indicate that the usually accepted value of about 208 kg.-cals. per mol. is some 20% too large; from spectroscopic measurements, R. S. Mulliken[3] gets 168·3 kg.-cals., and G. Herzberg and H. Sponer[4] find an almost identical value of 169·3. N. V. S.

5. Chemical Kinetics.

A chemical change within a molecule or between two molecules involves electronic transitions which are subject to the quantum laws. The point has now been reached in the development of the subject of reaction velocity where a beginning can be made in the interpretation of experimental data on wave-mechanical principles; conversely, it appears not unlikely that the chemical data on more complex molecules may assist the physicist in arranging energy states which are too complicated for mathematical treatment.

By a new graphical illustration applied to simple types of molecule, such as Y-shaped ones XR_2, J. E. Lennard-Jones[1] has shown how the physicist can picture the dissociation of the molecule into

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[3] *Physical Rev.*, 1934, **46**, 144.

[4] *Z. physikal. Chem.*, 1934, [*B*], **26**, 1; *A.*, 950.

[1] *Proc. Roy. Soc.*, 1934, [*A*], **146**, 242.

$X + R_2$ or $X + R + R$. The products and the probability of the decomposition are seen to depend on the energy. Of the greatest interest in this connexion is the demonstration of F. Patat[2] that the formaldehyde molecule decomposes photochemically into $CO + H_2$ in the longer-wave region of the absorption band, but gives hydrogen atoms in the shorter-wave region. These results are in qualitative agreement with the most recent interpretation of the absorption spectrum of gaseous formaldehyde.[3] It is not yet possible to form so clear a picture of the photochemical decomposition of more complex carbonyl compounds. The keten molecule, $CH_2{=}CO$, decomposes photochemically into carbon monoxide and ethylene apparently by a predissociation process :[4]

$$CH_2{=}CO + h\nu \longrightarrow CH_2{=}CO^{\times} \longrightarrow CH_2 \;{=}CO \longrightarrow CH_2 + CO,$$

but the nature of the excited levels involved awaits explanation. The homogeneous thermal decomposition of this molecule is of a complex nature.[5] Of greater difficulty is the interpretation of the photochemical decomposition of aldehydes and ketones. The spectra of acetaldehyde, propionaldehyde, and acetone each show two overlapping regions of absorption, the first being of discrete or diffuse structure, and the second continuous, as far as can be seen. This double structure is most clearly shown by acetone, where it appears that fluorescence takes place only from the discrete region, and not from the continuum.[6] A similar differentiation through fluorescence in the case of the other carbonyl compounds is less certain owing to overlapping of the regions. The excited levels involved, which we will call A levels, have not yet been interpreted, but they do not appear to be directly chemically reactive. In the *liquid* or *dissolved* states no gaseous photo-products are formed, but other chemical reactions occur with a quantum efficiency which is less the higher the concentration of the carbonyl compound.[7] Similar observations have been made in the case of dicarbonyl substances.[8] This is most readily explained by the non-reactivity of molecules in the primary excited levels A, their capability of deactivation by collision with normal molecules, and their passage (spontaneously or through collision with solvent molecules) into chemically reactive levels B. These reactive levels of ketone molecules in solution are powerful dehydrogenating agents, as shown by their action on alcohols. The alcohol is oxidised to aldehyde and the ketone molecule is reduced. If free oxygen is present, the alcohol is oxidised as before, but the ketone is not reduced. The mechanism of these reactions has been discussed by H. L. J. Bäckström.[9] The quinone molecule also possesses oxidising properties in its excited states.[10] In the *gaseous* state, owing to the slower collisional rates, the primary excited levels A of carbonyl and dicarbonyl compounds have time to pass (directly or indirectly) into other levels, C, which form gaseous products by unimolecular decompositions.[11]

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[2] *Z. physikal. Chem.*, 1934, [*B*], **25**, 208; *A.*, 740.

[3] G. H. Dieke and G. B. Kistiakowsky, *Physical Rev.*, 1934, **45**, 4.

[4] R. G. W. Norrish, H. G. Crone, and (Miss) O. Saltmarsh, *J.*, 1933, 1533; *A.*, 1934, 156; see also *A.*, 976; W. F. Ross and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 1112; *A.*, 740.

[5] A. T. Williamson, *ibid.*, 1934, **56**, 2216.

[6] R. G. W. Norrish, H. G. Crone, and O. D. Saltmarsh, *J.*, 1934, 1456; *A.*, 1184; C. F. Fisk and W. A. Noyes, *J. Chem. Physics*, 1934, **2**, 654; W. A. Noyes, A. B. F. Duncan, and W. M. Manning, *ibid.*, p. 717.

[7] E. J. Bowen and E. L. A. E. de la Praudière, *J.*, 1934, 1503.

[8] E. J. Bowen and A. T. Horton, *ibid.*, p. 1505.

T. G. Pearson [12] has shown, by the use of metallic mirrors, that free methyl groups are probably produced in this photodecomposition of gaseous acetone, methyl ethyl ketone, and diethyl ketone, but that neither methyl groups nor free hydrogen atoms are produced from acetaldehyde, propionaldehyde, or methyl butyl ketone. At temperatures above 80°, however, the kinetics of the photolysis of acetaldehyde change completely, chains being set up, and the rate becoming proportional to the square root of the light intensity.[13]

Under these conditions methyl radicals may take part in the chain mechanism. These radicals are incapable of initiating chains in acetone at temperatures below 400°, so that the photodecomposition at ordinary temperature is probably not a chain reaction.[14] Further work is still required before a composite picture can be presented of the photoreactions of carbonyl compounds. One of the difficulties is to account for the apparently continuous absorption spectra of these substances even at low pressures, which can hardly be due to photodissociation, since the quantum efficiency is less than unity.

Reference may also be made to another photochemical reaction which illustrates how chemical investigation may provide some information about the nature of an excited level. The photo-oxidation of rubrene [15] is not a chain reaction, as are so many oxidations, and is inhibited, not by "anti-oxygens," but by bases. This may indicate that the reactive level is of the nature of an acid, having a loosened proton rather than a loosened hydrogen atom.

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[9] *Z. physikal. Chem.*, 1934, [*B*], **25**, 99; *A.*, 611.

[10] A. Berthoud and D. Porret, *Helv. Chim. Acta*, 1934, **17**, 694; D. Porret, *ibid.*, p. 703; *A.*, 976.

[11] R. G. W. Norrish and M. E. S. Appleyard, *J.*, 1934, 847; *A.*, 852; cf. *Ann. Reports*, 1933, **30**, 48; 1932, **29**, 48.

[12] *J.*, 1934, 1718.

[13] J. A. Leermakers, *J. Amer. Chem. Soc.*, 1934, **56**, 1537; *A.*, 976.

[14] *Idem, ibid.*, p. 1899; *A.*, 1184; F. O. Rice, E. L. Rodowskas, and W. R. Lewis, *ibid.*, p. 2497.

[15] E. J. Bowen and F. Steadman, *J.*, 1934, 1098; *A.*, 977; see *Ann. Reports*, 1932, **29**, 173.

The concept of a limited number of different activated states, each with its own specific reactivity, in unimolecular thermal gaseous reactions, recently put forward by C. N. Hinshelwood [16] has been found to afford a good explanation of the kinetics of the decompositions of the series of molecules H·CHO, CH_3·CHO, C_2H_5·CHO, and CCl_3·CHO.[17] The hypothesis can be pictured as the production of reactivity through the elongation by vibration of a particular bond by different types of interference between the normal modes of vibration of the molecule.[18] The action of hydrogen in maintaining the supply of active molecules in the unimolecular thermal decomposition of acetaldehyde is such that no one activated state is favoured rather than another.[19] Experiments on the decomposition of diethyl ether at pressures up to 200 atmospheres seem to indicate that the number of degrees of freedom concerned in the mechanism of a unimolecular reaction may vary with the time between collisions.[20]

The free acceptance and development of these conceptions has been complicated by a view which has recently been advanced [21] that the decompositions by heat of the vapours of many organic compounds are chain reactions involving the formation of free radicals. The evidence for this is founded on the nature of the products of decomposition, on the kinetics,[22] and on the removal of metallic mirrors.[23] The thermal decomposition of dimethyl ether is accelerated by the introduction of methyl radicals from the photodecomposition of acetone,[24] and the methylene radical has been recognised in the decomposition of diazomethane in presence of ether.[25] A little azomethane mixed with the vapour of acetaldehyde at 300° brings about an acceleration of the decomposition of the latter.[26] This has been explained as the initiation of chains by methyl radicals derived from the azomethane. It must be remembered, however, that the thermal decomposition of aldehydes is catalysed by many substances, particularly by molecules of high polarisability such as iodine or hydrogen sulphide.[27] The general conclusion that long chains are set up in the decomposition of organic molecules must be regarded as provisional (see p. 48 for effect of methyl radicals on acetone). The reactions do not show the features commonly associated with chain reactions, such as inhibiting effects, wall effects, and complicated kinetics. There are other uncertainties of an experimental nature. Traces of oxygen may profoundly modify the kinetics of the decomposition reactions. In the thermal decomposition of acetaldehyde, a little oxygen increases the normal decomposition by as much as 1600 molecules for each oxygen molecule present.[28]

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[16] See *Ann. Reports*, 1933, **30**, 40.

[17] C. N. Hinshelwood, C. J. M. Fletcher, F. H. Verhoek, and C. A. Winkler, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 327; see also the case of N_2O, E. Hunter, *ibid.*, **144**, 386; *A.*, 603.

[18] M. Polanyi, *ibid.*, **146**, 253.

[19] C. J. M. Fletcher and C. N. Hinshelwood, *Trans. Faraday Soc.*, 1934, **30**, 614; *A.*, 969.

[20] E. W. R. Steacie and E. Solomon, *J. Chem. Physics*, 1934, **2**, 503; *A.*, 1179.

[21] F. O. Rice, *Trans. Faraday Soc.*, 1934, **30**, 152; *Ann. Reports*, 1933, **30**, 48.

[22] F. O. Rice and K. F. Herzfeld, *J. Amer. Chem. Soc.*, 1934, **56**, 284; *A.*, 369.

[23] F. O. Rice and F. R. Whaley, *ibid.*, p. 1311; *A.*, 863.

[24] J. A. Leermakers, *ibid.*, p. 1899; *A.*, 1184.

[25] F. O. Rice and A. L. Glasebrook, *ibid.*, p. 2381.

An acceleration due to traces of oxygen is also observed in *polymerisation* reactions, as in the case of ethylene.[29] Until further work is carried out, the detailed interpretations of the mechanisms of the *decompositions* of vapours of organic substances such as aliphatic hydrocarbons,[30] ethers,[31] alkyl nitrites,[32] aldehydes,[33] tertiary alcohols,[34] and possibly even of the *polymerisations* of unsaturated hydrocarbons[35] must remain uncertain. Careful reinvestigation of many of the above reactions with the special purpose of deciding the nature of the mechanism is urgently required.

[26] D. V. Sickman and A. O. Allen, *J. Amer. Chem. Soc.*, 1934, **56**, 1251, 2031; *A.*, 758.

[27] S. Bairstow and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1933, [*A*], **142**, 77; *A.*, 1933, 1251; H. Fromherz, *Z. physikal. Chem.*, 1934, [*B*], **25**, 301; *A.*, 737.

[28] Letort, *Compt. rend.*, 1933, **197**, 1642; 1934, **199**, 351; *A.*, 1934, 38, 1073.

[29] H. H. Storch, *J. Amer. Chem. Soc.*, 1934, **56**, 374; *A.*, 369.

[30] W. A. Bone, *Trans. Faraday Soc.*, 1934, **30**, 148; A. I. Dintzess, *Compt. rend. Acad. Sci. U.R.S.S.*, 1933, **4**, 153; *A.*, 1934, 259; A. I. Dintzess and A. V. Frost, *J. Gen. Chem. Russ.*, 1933, **3**, 747; *A.*, 1934, 151; R. E. Paul and L. F. Marck, *Ind. Eng. Chem.*, 1934, **26**, 454; *A.*, 603.

[31] W. Ure and J. T. Young, *J. Physical Chem.*, 1933, **37**, 1169, 1183; *A.*, 1934, 261; O. K. Rice and D. V. Sickman, *J. Amer. Chem. Soc.*, 1934, **56**, 1444; *A.*, 969.

[32] E. W. R. Steacie and G. T. Shaw, *J. Chem. Physics*, 1934, **2**, 345; *A.*, 847.

[33] C. C. Coffin, *Canadian J. Res.*, 1933, **9**, 603; *A.*, 1934, 368; C. C. Coffin and A. L. Geddes, *J. Chem. Physics*, 1934, **2**, 47; *A.*, 259; *Canadian J. Res.*, 1934, **11**, 180; *A.*, 1179; L. S. Kassel, *J. Chem. Physics*, 1934, **2**, 106; *A.*, 368.

[34] R. F. Schultz and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 395; *A.*, 369.

[35] W. E. Vaughan, *ibid.*, 1933, **55**, 4109; *A.*, 1933, 1249; T. S. Chambers and G. B. Kistiakowsky, *ibid.*, 1934, **56**, 399; *A.*, 369; M. V. Krauze, M. S. Nemtzov, and E. A. Soskina, *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **3**, 262; *A.*, 1179.

New measurements of the quantum efficiency of the photo-isomerisation of the *o*-nitrobenzaldehydes to *o*-nitrosobenzoic acids show that its value is about 0·5, both in the dissolved and in the solid state, results which are in agreement with earlier work.[36] From a consideration of the structure and of the nature of the energy surfaces of the molecule, it is concluded that the reason for this value is the approximate equality between the times of deactivation and reactivation. It may be that if the N–O bond in the nitro-group next to the aldehyde group is excited, reaction almost always occurs, while if the further bond is excited, deactivation takes place. If this is so, a new field connecting stereochemistry and photochemistry may be opened up.

In a molecule which has more than one light-absorbing centre it is possible by varying the wave-length to excite it at different points. The photochemical reactions of such molecules are naturally of great interest. An example of this is found in *trans*-stilbene,[37] which changes into the *cis*-form with a quantum efficiency of unity when irradiated with ultra-violet light of 3135 Å.; the excitation being of the ethylene linkage, and probably changing the double bond into something approaching a single bond, so permitting of rotation. In the shorter ultra-violet region is another absorption band, probably associated with excitation of the aromatic part of the molecule. The quantum efficiency of the change in light of this region is 0·4. How the excitation energy is transferred from aromatic nucleus to ethylene linkage, whether by collision, internal rearrangement of energy within one molecule, or through fluorescence, is not known.

Another problem of the greatest interest is that of " normal " and " slow " reactions in solution. It is now generally accepted that collisional frequencies between molecules in dilute solution in a liquid are not very different from those in a gas at the same concentration.[38] In the expression for the rate of a chemical reaction, *viz.*, rate $= PZe^{-E/RT}$, where $E =$ heat of activation, $Z =$ collisional number, and $P =$ probability that reaction will occur if the energy exceeds E, many reactions have a value of P not far from unity, and this is generally the case for reactions involving the substitution of a negative group by a negative ion, as in the reaction $R_1R_2R_3CCl + OH' \longrightarrow R_1R_2R_3C{\cdot}OH + Cl'$. The rate of such reactions is given approximately by the expression $k_{(\mathrm{mol./litre})} = 10^{10}e^{-E/RT}$, the only variable being the value of the heat of activation E. M. Polanyi [39] has developed a simple picture of the mechanism of these reactions which shows that optical inversion is always to be expected, and that the heat of activation depends on the force constants within the molecule. The phenomena of the "Walden inversion" and of "stereo-hindrance" are thus rendered more intelligible.

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[36] P. A. Leighton and F. A. Lucy, *J. Chem. Physics*, 1934, **2**, 756, 761; F. Weigert and L. Brodmann, *Trans. Faraday Soc.*, 1926, **21**, 453; *A.*, 1925, ii, 1075; E. J. Bowen, (Sir) H. B. Hartley, W. D. Scott, and H. G. Watts, *J.*, 1924, **125**, 1218.

[37] A. Smakula, *Z. physikal. Chem.*, 1934, [*B*], **25**, 90; *A.*, 611.

[38] E. A. Moelwyn-Hughes, *Chem. Reviews*, 1932, **10**, 241.

For certain other types of reactions in solution the probability factor P is very low, sometimes reaching values of 10^{-6} to 10^{-7}.[40] Such low efficiencies of reaction cannot be explained by the deactivating influence of the solvent, but may arise from the necessity for a certain orientation during collision, for a certain distribution within the molecules of the energy of activation, from an "ionic" mechanism, or from other causes.[41]

It is well known that the rates of bimolecular organic reactions are greatly influenced by changes in the substituents in the reacting molecules,[42] and an interesting study has been made on the reaction in benzene solution between substituted benzoyl chlorides and substituted anilines.[43] It appears that the changes in the rates of reaction due to changes in the substituents of the reacting molecules are chiefly due to changes in the heats of activation of the reactions,[44] and not to changes in the probability factor, which has the low value of about 10^{-7}. The effect of substituents in this reaction is thus similar to that found by A. E. Bradfield and his co-workers [45] for the rates of chlorination of phenyl and tolyl ethers. These remarkable results were certainly unexpected, and show that in spite of the number of hypothetical reasons for the "slowness" of these reactions, all of which might be operating together, in certain reactions an unforeseen simplicity emerges. Of the possibilities mentioned above, the factor which appears the most constant is that of orientation, but it is premature to say that this is the chief reason for the "slowness" of these reactions. Another aspect of the problem remains to be explored. These "slow" reactions are very susceptible to solvent influence, and go much faster in solvents of high dipole moment. They are probably, in fact, not bimolecular but termolecular, a collision with a solvent molecule being necessary for reaction. Such a necessity may arise if the wave functions of the original and the reacted forms of the bimolecular complex are of different symmetry; transitions will then be possible only through perturbations due to the electric field of solvent molecules in the near neighbourhood.[46] There are experimental indications, but little more at present, that the effect of the solvent on " slow " reactions is to alter the probability factor P, as expected on the above considerations.

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[39] *Proc. Roy. Soc.*, 1934, [*B*], **116**, 202; *Mem. Manchester Lit. Phil. Soc.*, 1934, **41**, 41.

[40] See *Ann. Reports*, 1932, **29**, 42; Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 3rd edn., Oxford, 1933, p. 230.

[41] *Idem*, *J.*, 1934, 1357; *A.*, 1248.

[42] See *Ann. Reports*, 1933, **30**, 42.

[43] E. G. Williams and C. N. Hinshelwood, *J.*, 1934, 1079; *A.*, 971.

[44] See H. A. C. McKay, *J. Soc. Chem. Ind.*, 1934, **53**, 870.

[45] A. E. Bradfield, W. O. Jones, and F. Spencer, *J.*, 1931, 2907; *A.*, 1932, 26; *Chem. and Ind.*, 1932, 254.

The process of esterification is a " slow " reaction, and needs a third catalyst molecule. In ester formation between acetic acid and methyl alcohol, the probability factor P is 10^{-7} when the catalyst molecule is another undissociated acetic acid molecule, but is 10^{-3} when the catalyst is the hydrogen ion.[47] An investigation of the acetone–iodine reaction, which similarly needs a catalyst molecule, has shown that the probability factors for the reaction proceeding under the influence of different catalysts vary considerably, and are related to the acid strength of the catalyst molecule.[48] From this it appears that the polarisation, if not the ionisation, of the catalyst molecule is an essential condition for reaction, as expected from the above wave-mechanical considerations.

Miscellaneous Reactions.—The reaction between hydrogen and oxygen has been investigated under new conditions. In the Schumann region of the ultra-violet, oxygen molecules are dissociated into normal ^3P and metastable ^1D atoms, and the latter are found to react with hydrogen much more rapidly than the former.[49] To avoid the use of waxed-on fluorite plates for work in this region, very thin (10 μ) bubble-shaped windows of quartz were used.[50] The mercury-sensitised reaction between hydrogen and oxygen, where the hydrogen is dissociated, has been investigated by measuring the stationary atom concentration through the ortho–para hydrogen change.[51] The reactions $H + O_2 \longrightarrow HO_2$ (and $H + CO \longrightarrow HCO$) are thereby found to be three-body collisional processes. There is little difference in rate between the mercury-sensitised reactions of hydrogen and deuterium with oxygen, where the process is an atomic one.[52] The thermal chain reactions between these substances have different rates at pressures above the upper explosion limit, and have different upper limits.[53] The quantitative interpretation of these effects affords a means of choosing between different possibilities of chain branching and ending.[54]

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[46] C. Zener, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 254; J. E. Lennard-Jones, *ibid.*, p. 242.

[47] C. N. Hinshelwood and A. T. Williamson, *Trans. Faraday Soc.*, 1934, **30**, 1145; A. C. Rolfe and C. N. Hinshelwood, *ibid.*, p. 935; *A.*, 1180.

[48] G. F. Smith, *J.*, 1934, 1744.

[49] H. Neujmin and B. Popov, *Z. physikal. Chem.*, 1934, [*B*], **27**, 15.

[50] Cf. *Z. Physik*, 1932, **76**, 322.

[51] L. Farkas and H. Sachsse, *Z. physikal. Chem.*, 1934, [*B*], **27**, 111.

The mechanism of the photodecomposition of gaseous ammonia by light of wave-length about 2100 Å. has been further investigated by the use of the new forms of hydrogen. The primary process appears to be $NH_3 + h\nu \longrightarrow NH_2 + H$ (through predissociation), but the low quantum efficiency (about 0·25) indicates some kind of back reaction.[55] L. Farkas and P. Harteck [56] have measured the stationary hydrogen-atom concentration during illumination by means of the ortho–para hydrogen change. From the variation of this concentration with temperature, pressure, and light intensity, they conclude that the atoms largely combine with ammonia to give NH_4, which can then re-form ammonia or decompose by secondary reactions. If this is so, the complex NH_4 cannot have four equivalent N–H linkages, *i.e.*, it must be NH_3–H, since H. S. Taylor and J. C. Jungers [57] have shown that when gaseous ammonia is illuminated in presence of deuterium, the reaction $NH_3 + D \longrightarrow NH_2D + H$ does not readily take place. An equilibrium mixture of the deuteroammonias, NH_2D, NHD_2, and ND_3, recognisable by their different absorption spectra, is actually produced on illumination of ammonia-deuterium mixtures, but through a mechanism involving the preliminary decomposition of the ammonia, followed by the reaction $NH_2 + D_2 \longrightarrow$ deuteroammonias. Further quantitative examination of the problem by the newer technique is still required.

The mercury-sensitised photodecompositions of ammonia and of trideuteroammonia have been compared,[58] that of the latter being more than ten times slower than the former. Although it is not yet possible to explain the mechanism in detail, the results already show that the quenching of the excited mercury atom by the ammonia molecule only rarely leads to photosensitised decomposition, *i.e.*, most of the $^3P_1$ mercury atoms pass to the $^3P_0$ state, transferring an energy inadequate to decompose the ammonia molecule. The quenching ratio of $NH_3 : ND_3$ is 4 : 1.

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[52] M. G. Evans, *J. Chem. Physics*, 1934, **2**, 726; H. W. Melville, *Nature*, 1934, **133**, 947.

[53] C. N. Hinshelwood, A. T. Williamson, and J. H. Wolfenden, *ibid.*, p. 836; *A.*, 736.

[54] See C. N. Hinshelwood and A. T. Williamson, "The Reaction between Hydrogen and Oxygen," Oxford, 1934.

[55] R. A. Ogg, P. A. Leighton, and F. W. Bergstrom, *J. Amer. Chem. Soc.*, 1934, **56**, 318; *A.*, 374.

[56] *Z. physikal. Chem.*, 1934, [*B*], **25**, 257; *A.*, 739.

[57] *J. Chem. Physics*, 1934, **2**, 452.

[58] J. C. Jungers and H. S. Taylor, *ibid.*, p. 373; *A.*, 1078; M. G. Evans and H. S. Taylor, *ibid.*, p. 732.

Recent work on the photochemical reactions between chlorine and hydrogen, carbon monoxide, or methane [59] has been directed towards a more quantitative knowledge of the mechanisms of chain propagation and ending.[60] The chain carrier is probably Cl_3 rather than Cl.[61] The kinetics of the hydrogen–chlorine reaction in presence of a large excess of oxygen show that the chain-ending process is $H + O_2 \longrightarrow HO_2$.[62] The first step, $Cl + H_2 \longrightarrow HCl + H$, does not occur on every collision, but needs activation energy, and owing to the difference in zero-point energies of the two isotopes of hydrogen, the molecule D_2 reacts at ordinary temperature only one-third as rapidly as the molecule H_2.[63] A similar difference in rate, for the same reason, is found in the thermal reactions of bromine with hydrogen or deuterium.[64]

Investigations have been made of the photokinetics of a number of reactions whose rate is proportional to the square root of the light intensity : the photohalogenation of cinnamic acid,[65] the reaction in the gas phase between chlorine and trichlorobromomethane,[66] and the reaction between chlorine and chloroform.[67] The photobromination of acetylene is a very sensitive chain reaction.[68] Reference may also be made to the following photoreactions which have recently been examined : the decomposition of solid lithium hydride,[69] the oxidation of mercury vapour,[70] the photolysis of silver halides,[71] of metallic carbonyls,[72] of the oxides of nitrogen,[73] of chlorine dioxide,[74] of ozone,[75] of mixtures of chlorine and ozone,[76] of liquid ethyl iodide,[77] of the photo-oxidation of ethyl iodide,[78] and of the effect of inhibitors on the decomposition of hydrogen peroxide.[79]

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[59] L. T. Jones and J. R. Bates, *J. Amer. Chem. Soc.*, 1934, **56**, 2282.

[60] See *Ann. Reports*, 1933, **30**, 49.

[61] G. K. Rollefson, *J. Amer. Chem. Soc.*, 1934, **56**, 574; *A.*, 496.

[62] K. B. Krauskopf and G. K. Rollefson, *ibid.*, p. 327; *A.*, 374; see also the effect of oxygen on the thermal hydrogen–chlorine reaction, R. N. Pease, *ibid.*, p. 2388.

[63] L. Farkas and A. Farkas, *Naturwiss.*, 1934, **22**, 218; *A.*, 602; G. K. Rollefson, *J. Chem. Physics*, 1934, **2**, 144; *A.*, 610.

[64] F. Bach, K. F. Bonhoeffer, and E. A. Moelwyn-Hughes, *Z. physikal. Chem.*, 1934, [*B*], **27**, 71.

[65] A. Berthoud and D. Porret, *Helv. Chim. Acta*, 1934, **17**, 237; *A.*, 496; W. H. Bauer and F. Daniels, *J. Amer. Chem. Soc.*, 1934, **56**, 378; *A.*, 374.

[66] H. G. Vesper and G. K. Rollefson, *ibid.*, p. 1455; *A.*, 976.

[67] H. J. Schumacher and K. Wolff, *Z. physikal. Chem.*, 1934, [*B*], **25**, 161; *A.*, 740; cf. A. T. Chapman, *J. Amer. Chem. Soc.*, 1934, **56**, 818; *A.*, 611.

[68] J. E. Booker and G. K. Rollefson, *ibid.*, p. 2288.

[69] F. Bach and K. F. Bonhoeffer, *Z. physikal. Chem.*, 1933, [*B*], **23**, 256; *A.*, 1934, 7.

[70] J. M. Frank, *Compt. rend. Acad. Sci. U.R.S.S.*, 1933, **4**, 146; *A.*, 1934, 263.

The technique of actinometry in the ultra-violet has now been developed so as to be the most convenient method of measuring radiation for photochemical purposes.[80]

A new method of measuring very high-velocity gas reactions[81] consists in introducing n atoms per second of a gas such as sodium vapour into the reacting gas such as a methyl halide at a concentration c, and measuring by light-absorption methods the number N of atoms of sodium in the stationary reaction zone (*i.e.*, the flame). The velocity constant is then simply nc/N. This method is more reliable than earlier ones for measuring the fastest reactions. A streaming method has been applied to investigate the very rapid reaction between sulphur trioxide and water in the vapour phase.[82] The Hartridge–Roughton method of measuring fast reactions has been applied to an extensive investigation of the reactivity of hæmoglobin towards oxygen and carbon monoxide.[83] The chain mechanisms of the autoxidations of solutions of sulphites and of aldehydes have been discussed in the light of recent work.[84] The thermal decomposition of fluorine monoxide provides an example of a reaction in which the life of the activated molecule is so short that practically every activated molecule decomposes under ordinary conditions of pressure.[85] A further examination of the reaction between hydrogen and sulphur vapour has led to results in disagreement with earlier work.[86] The mechanism of combination of hydrogen atoms in the gaseous phase is through triple collisions, and interesting results have been obtained on the efficiency of the process.[87] In the homogeneous thermal decomposition of carbon suboxide, C_3O_2, at 200°, dicarbon gas, C_2, is supposed to be formed as a carmine-red vapour which rapidly polymerises to a purple-red solid variety of carbon.[88]

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[71] P. Feldman and A. Stern, *Z. physikal. Chem.*, 1934, [*B*], **26**, 45; *A.*, 976.

[72] H. W. Thompson and A. P. Garratt, *J.*, 1934, 524, 1817; *A.*, 582; A. Terenin, *J. Chem. Physics*, 1934, **2**, 441; *A.*, 940.

[73] H. H. Holmes and F. Daniels, *J. Amer. Chem. Soc.*, 1934, **56**, 630; *A.*, 496.

[74] J. W. T. Spinks and J. M. Porter, *ibid.*, p. 264; *A.*, 374.

[75] L. J. Heidt and G. S. Forbes, *ibid.*, p. 2365.

[76] A. C. Byrns and G. K. Rollefson, *ibid.*, p. 2245.

[77] B. M. Norton, *ibid.*, p. 2294.

[78] L. T. Jones and J. R. Bates, *ibid.*, p. 2285.

[79] D. Richter, *J.*, 1934, 1219; *A.*, 1075.

[80] F. P. Brackett and G. S. Forbes, *J. Amer. Chem. Soc.*, 1933, **55**, 4459; *A.*, 1934, 40; G. S. Forbes and L. J. Heidt, *ibid.*, p. 2363; L. Farkas, *Z. physikal. Chem.*, 1933, [*B*], **23**, 89; *A.*, 1933, 1255.

[81] L. Frommer and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 519; *A.*, 969.

[82] C. F. Goodeve, A. S. Eastman, and A. Dooley, *ibid.*, p. 1127.

[83] F. J. W. Roughton, *Proc. Roy. Soc.*, 1934, [*B*], **115**, 451; *A.*, 1073; see also *ibid.*, **116**, 192, 198.

[84] H. L. J. Bäckström, *Z. physikal. Chem.*, 1934, [*B*], **25**, 99, 122; *A.*, 611; see also G. E. K. Branch, H. J. Almquist, and E. C. Goldsworthy, *J. Amer. Chem. Soc.*, **1933**, **55**, 4052; *A.*, 1252.

An extremely interesting use has been made of the isotope of oxygen O^{18} to decide whether the bond between oxygen and alkyl or acyl is split in the hydrolysis of esters by alkali.[89] Amyl acetate was hydrolysed by alkali in water containing more than the usual amount of O^{18}, and the question whether the O^{18} goes to the acid or the alcohol was investigated, the result showing that the acyl–oxygen bond is the one which breaks. The experiments also show, incidentally, that no interchange takes place between hydroxyl ions and the hydroxyl group of the alcohol; *i.e.*, alcohols which are known to ionise giving hydrogen ions do not appreciably ionise in another way giving hydroxyl ions. The hydrogen isotope has been used to investigate the mechanism of interchange of hydrogen atoms between hydrocarbons and hydrogen in presence of metallic catalysts, *i.e.*, to throw light on the actual mechanism of processes of hydrogenation.[90]

The method of investigation of films by means of their surface potentials has been applied by E. K. Rideal and his co-workers to the measurement of reaction velocities in unimolecular films. The molecular statistics of the hydrolysis of a film of stearolactone by hydroxyl ions closely resemble those for similar reactions in homogeneous solution.[91] Vitamin-*D* appears to be formed on irradiation of films of ergosterol.[92] The rate of oxidation of unimolecular films of unsaturated acids by dilute solutions of permanganate depends on the degree of extension of the film, the rate diminishing when the unsaturated linkings are removed from the surface by compression.[93] Experiments of great interest in biochemistry have been carried out on the rates of digestion of monolayers of proteins by enzymes.[94] In certain cases the rate of attack of enzymes on protein films is inhibited by compression of the film, an observation which seems paralleled by the behaviour of the metabolism of resting muscle, which rises when the muscle is maintained in a stretched condition.[95]

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[85] W. Koblitz and H. J. Schumacher, *Z. physikal. Chem.*, 1934, [*B*], **25**, 283; *A.*, 736.

[86] E. E. Aynsley and P. L. Robinson, *Nature*, 1934, **133**, 723; *A.*, 737.

[87] H. M. Smallwood, *J. Amer. Chem. Soc.*, 1934, **56**, 1542; *A.*, 969.

[88] A. Klemenc, *Z. Elektrochem.*, 1934, **40**, 488; *A.*, 969.

[89] M. Polanyi and A. L. Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508.

[90] Iurô Horiuti and M. Polanyi, *ibid.*, p. 1164.

[91] R. J. Fosbinder and E. K. Rideal, *Proc. Roy. Soc.*, 1933, [*A*], **143**, 61.

[92] R. J. Fosbinder, *ibid.*, **139**, 93; *A.*, 1933, 326.

[93] A. H. Hughes and E. K. Rideal, *ibid.*, **140**, 253; *A.*, 1933, 679.

E. J. B.

6. ELECTROLYTES.

Theoretical interest in this field still centres mainly on the applicability of a simplified electrostatic model to account for the properties of ionic solutions, and the chief features to report are the application of this model to a larger number of problems, the accumulation of a considerable amount of accurate data for very dilute solutions, and attempts to extend the theory to more concentrated solutions.

The thermodynamic properties of an ionic solution can all be described in terms of the free energy, and the electrostatic theory gives as the limiting law in dilute solutions

$$F_e = -(\sum_i N_i z_i^2)^{3/2} 2\varepsilon^3\sqrt{\pi}/3D^{3/2}\sqrt{kTV} \quad . \quad . \quad (1)$$

where F_e is the electrical contribution to the free energy of a solution of dielectric constant D containing N_i ions of charge $z_i\varepsilon$ in volume V. This expression is equivalent to the limiting law for activity coefficients (or osmotic coefficients) which was discussed in these Reports last year.[1] Mention may, however, be made of a series of accurate freezing-point measurements for 25 uni-univalent salts in aqueous solution.[2] Treatment of these data by the method of least squares (to avoid errors of personal judgment or prejudice) shows that the limiting slope certainly does not differ from the theoretical value by more than 10%.[3] The same conclusion is reached by J. Lange[4] from his cryoscopic measurements on tetra-alkylammonium halides.

Differentiation of equation (1) with respect to temperature or pressure leads to expressions for other properties of the solution which may be used to test the theory and are actually found to be much more sensitive to deviations than the activity coefficients.

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[94] J. H. Schulman and E. K. Rideal, *Biochem. J.*, 1933, **27**, 1581; *A.*, 1933, 1331.

[95] See E. K. Rideal, *Proc. Roy. Soc.*, 1934, [*B*], **116**, 200.

[1] *Ann. Reports*, 1933, **30**, 21.

[2] G. Scatchard, S. S. Prentiss, and P. T. Jones, *J. Amer. Chem. Soc.*, 1932, **54**, 2690; *A.*, 1932, 912; *ibid.*, 1934, **56**, 805; *A.*, 596; Scatchard and Prentiss, *ibid.*, 1932, **54**, 2696; *A.*, 1932, 912; *ibid.*, 1933, **55**, 4355; *A.*, 1934, 25; *ibid.*, 1934, **56**, 807; *A.*, 596.

[3] S. S. Prentiss and G. Scatchard, *Chem. Reviews*, 1933, **13**, 139.

[4] *Z. physikal. Chem.*, 1934, [*A*], **168**, 147; *A.*, 596.

One differentiation with respect to T gives the heat of dilution; this subject has been recently discussed in these reports,[5] since when no fundamental advances have been made. One differentiation with respect to pressure gives an expression for the variation of the partial molal volume of the electrolyte with concentration, first derived theoretically by O. Redlich and P. Rosenfeldt.[6] The theory predicts that in dilute solutions the partial molal volume should be a linear function of $\sqrt{c}$, and that the slope of this line should depend only on the properties of the solvent and the valency type of the electrolyte. It is difficult to carry out density measurements at sufficiently great dilutions for a satisfactory test, but work by W. Geffcken and D. Price [7] on uni-uni- and uni-bi-valent salts in water gives results which tend to approach the theoretical line at high dilutions. The application of the theory to other solvents is rendered difficult by uncertainty as to the value of the pressure coefficient $\partial D/\partial P$, but the results of Butler [8] for methyl-alcoholic solutions are at least compatible with the theory. A still unexplained and striking fact is that the results for high concentrations (0·1—3N) conform accurately to a square-root law, but with a different slope for each salt.

Two differentiations of equation (1) with respect to T give the specific heat of the electrolyte solution,[9] two differentiations with respect to P its compressibility,[10] and successive differentiations with respect to T and P its thermal expansibility.[11] (In each case we obtain the variation of the corresponding partial molal quantity with the concentration.) The expressions thus obtained involve the coefficients $\partial^2D/\partial T^2$, $\partial^2D/\partial P^2$, and $\partial^2D/\partial T\partial P$, which are not at present known with any certainty, and it is thus impossible to make a complete quantitative test. However, in each case the theory predicts a linear variation with $\sqrt{c}$, with a slope proportional to the valency factor $(\Sigma\nu_iz_i^2)^{3/2}$, and otherwise depending only on the properties of the solvent. Some experimental work has been done recently on the determination of the specific heats,[12] compressibilities,[13] and thermal expansion [14] of electrolyte solutions, and F. T. Gucker [10] has reviewed the available data. Although the solutions were, in general, much too concentrated for the simple Debye–Hückel picture to apply, a square-root relation was found to hold in all cases, but with individual slopes for the different electrolytes. These slopes are of the predicted order of magnitude, and change with the valency type roughly as predicted by the theory, but the experimental points show no signs of approaching a common slope for all electrolytes of the same type. It may be a significant fact that if the solutes are arranged in order of increasing slope of the $\bar{v}$–$\sqrt{c}$ curve, the slopes for the other properties follow almost the same order, indicating the presence of some factor not accounted for by the electrostatic theory which affects all the properties in the same way. It is, however, disconcerting to find that the partial molal volumes and compressibilities of urea and sucrose in aqueous solution also exhibit a linear dependence on $\sqrt{c}$, since if this relation is general for non-electrolyte solutions it is obviously unjustifiable to attribute the behaviour of electrolytes primarily to the ionic atmosphere. More experimental work is needed.

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[5] *Ann. Reports*, 1932, **29**, 29—34.

[6] See *ibid.*, 1930, **27**, 29.

[7] *Z. physikal. Chem.*, 1934, [*B*], **26**, 81; *A.*, 959.

[8] W. C. Vosburgh, (Miss) L. C. Connell, and J. A. V. Butler, *J.*, 1933, 933.

[9] See V. K. LaMer and I. A. Cowperthwaite, *J. Amer. Chem. Soc.*, 1933, **55**, 1004; *A.*, 1933, 466; H. Hammerschmidt and E. Lange, *Z. physikal. Chem.*, 1932, [*A*], **160**, 445; *A.*, 1932, 913. It should be noted that in this case the omission of the terms involving $\partial v/\partial T$ and $\partial^2v/\partial T^2$ (as in the expression given by W. Lange and G. Messner, *Z. Elektrochem.*, 1927, **33**, 440; *A.*, 1928, 134; and by M. Randall and F. D. Rossini, *J. Amer. Chem. Soc.*, 1929, **51**, 323; *A.*, 1929, 398) introduces a much greater error than in the case of the heat of dilution (cf. *Ann. Reports*, 1932, **29**, 30, footnote), the error in water being about 16%.

[10] F. T. Gucker, *Chem. Reviews*, 1933, **13**, 111.

[11] *Idem*, *J. Amer. Chem. Soc.*, 1934, **56**, 1017; *A.*, 729.

The fundamental conceptions of the ionic atmosphere continue to be supported by work on non-stationary phenomena (conductivity, viscosity, and dispersion effects). L. Onsager and R. M. Fuoss [15] have given a general theoretical treatment of such irreversible processes which applies to the conductivity, viscosity, and diffusion of an arbitrary mixture of strong electrolytes. Since the last report on the conductivity of electrolytes [16] very accurate work has been done on aqueous solutions by T. Shedlovsky and his collaborators.[17] By means of an improved technique, it is now possible to measure the conductivity of 0·00003N-salt solutions with an accuracy of 0·02%, and it is satisfactory to find that up to about 0·001N the experimental results agree with the Onsager equation within this small experimental error. In particular, it may be noted that V. K. Sementschenko, B. V. Jerofejev, and V. V. Serpinski,[18] using the same technique, have found that magnesium sulphate agrees with the theory at sufficiently great dilutions. Older measurements on bi-bivalent salts at somewhat higher concentrations gave slopes about 100% higher than the theoretical, but it now appears certain that in all such cases the apparent straight line obtained is actually the middle section of a curve having a point of inflexion. Shedlovsky has also proposed an empirical extension of the Onsager equation : if the latter (for a uni-univalent electrolyte) is written in the form

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[12] T. W. Richards and M. Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 794; *A.*, 1929, 652; M. Randall and F. D. Rossini, *ibid.*, p. 323; *A.*, 1929, 398; F. T. Gucker and K. H. Schminke, *ibid.*, 1932, **54**, 1358; 1933, **55**, 1013; *A.*, 1932, 696; 1934, 466.

[13] E. P. Perman and W. D. Urry, *Proc. Roy. Soc.*, 1929, [*A*], **126**, 44; *A.*, 1930, 154; *ibid.*, 1934, [*A*], **146**, 640; *A.*, 1304. F. T. Gucker, *J. Amer. Chem. Soc.*, 1933, **55**, 2709; *A.*, 1933, 901; A. F. Scott, V. M. Obenaus, and R. W. Wilson, *J. Physical Chem.*, 1934, **38**, 931, 951.

[14] F. T. Gucker, *J. Amer. Chem. Soc.*, 1934, **56**, 1017; *A.*, 729.

[15] *J. Physical Chem.*, 1932, **36**, 2689; *A.*, 1933, 28.

[16] *Ann. Reports*, 1930, **27**, 326.

[17] T. Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1405; *A.*, 1932, 699; T. Shedlovsky and A. S. Brown, *ibid.*, 1934, **56**, 1066; *A.*, 735. Cf. also G. Jones and C. F. Bickford, *ibid.*, p. 602; *A.*, 491; J. Lange, *Z. physikal. Chem.*, 1934, **168**, 147; *A.*, 596; Shedlovsky, A. S. Brown, and D. A. McInnes, *Trans. Amer. Electrochem. Soc.*, 1934, **66**, 237; *A.*, 1308.

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + 2\beta)\sqrt{c} \quad . \quad . \quad . \quad . \quad (2)$$

then Shedlovsky's equation is

$$\Lambda_0 = (\Lambda + 2\beta\sqrt{c})/(1 - \alpha\sqrt{c}) - Bc \quad . \quad . \quad . \quad (3)$$

B being an empirical constant. If B is zero, it reduces to equation (2). This equation represents the experimental data better than any other equation with one empirical constant, and agrees with data for uni-univalent electrolytes up to nearly 0·1N. No theoretical basis for the equation has yet been found, but it may be significant that the value of B is always within 15% of $(\alpha\Lambda_0 + 2\beta)$.

Improved technique in the measurement of transport numbers by the moving-boundary method has raised the accuracy to about 0·02% in dilute solutions.[19] On the basis of equation (2) it is easily shown [20] that in dilute solutions the variation of the transport number of the anion (T_r) with concentration is given by

$$\operatorname*{Lim.}_{c \to 0}\left(\frac{dT_+}{d\sqrt{c}}\right) = \frac{(T_+{}^0 - 1)\beta}{2\Lambda_0} \quad . \quad . \quad . \quad . \quad (4)$$

$T_+{}^0$ being the value of the transport number at infinite dilution. This limiting relation agrees well with the experimental results, except for nitrates, which are known to be abnormal in several respects. By combining the results of conductivity and transport-number measurements, it is possible to obtain accurate values for the single ionic mobilities at different concentrations.[21] It is found that Kohlrausch's law of independent ionic mobilities is valid up to about $0{\cdot}01N$, nitrates again being an exception.

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[18] *Z. physikal. Chem.*, 1934, **167**, 188; *A.*, 257.

[19] For description of technique and full references, see D. A. McInnes and L. G. Longsworth, *Chem. Reviews*, 1932, **11**, 171.

[20] L. G. Longsworth, *J. Amer. Chem. Soc.*, 1932, **54**, 2741; *A.*, 1932, 914.

[21] D. A. McInnes, T. Shedlovsky, and L. G. Longsworth, *ibid.*, p. 2758; *A.*, 1932, 914.

The theory of the viscosity of strong electrolytes[22] has been further treated by H. Falkenhagen and E. Vernon[23] and the experimental technique improved by the electric timing device of G. Jones and S. K. Talley[24] and the differential method of W. M. Cox and J. H. Wolfenden.[25] If the viscosity is expressed in the form

$$\eta = \eta_0 (1 + A\sqrt{c} + Bc) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

η_0 being the viscosity of the pure solvent, then the value of A is predicted by the Falkenhagen–Dole theory. There is reasonable agreement between the experimental and the theoretical values[26] except for magnesium sulphate; this probably corresponds to the earlier discrepancies found for the conductivities of bi-bivalent electrolytes, and it may be anticipated that at still lower concentrations the theoretical relation will be obeyed. Agreement is also found for tetraethylammonium picrate in nitrobenzene, sodium iodide in ethyl alcohol, and lithium chloride in acetone.[27] Cox and Wolfenden have pointed out that the empirical constant B in equation (5) is made up additively of quantities characteristic of the anion and cation, which relation was further confirmed (with some exceptions) by V. D. Laurence and J. H. Wolfenden.[28] Jones and Talley have shown that A is zero for a non-electrolyte, as would be expected in the absence of ionic-atmosphere effects.

The theory of the dispersion of conductivity and dielectric constant[29] has been extended by H. Falkenhagen and W. Fischer,[30] while special points in the theory have been treated by M. Wien[31] and P. Debye.[32]

The experimental work on high-frequency conductivities has been extended by the use of methods involving a measurement of the heat developed, and the theory is in general confirmed.[33] The available data for the dielectric constant of electrolytes at high frequencies also agree reasonably with the theory.[34] It should, however, be noted that the majority of the above methods are only comparative, and give the difference between the dispersion effects for a standard uni-univalent electrolyte and the higher valency-type electrolyte being investigated. It is therefore disturbing to find that some direct measurements of the high-frequency conductivity and dielectric constant of uni-univalent electrolytes give results not agreeing with the theory.[35] In many cases the interpretation of the results is complicated by dipole absorption by the solvent.[36]

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[22] Cf. *Ann. Reports*, 1931, **28**, 33.

[23] *Phil. Mag.*, 1932, [vii], **14**, 537; *A.*, 1932, 1200.

[24] *J. Amer. Chem. Soc.*, 1933, **55**, 624; *A.*, 1933, 347.

[25] *Proc. Roy. Soc.*, 1934, [*A*], **145**, 475; *A.*, 959.

[26] See refs. (24) and (25); also H. M. Glass and W. M. Madgin, *J.*, 1934, 1124.

[27] Cox and Wolfenden, *loc. cit.*; G. R. Hood and L. P. Hohlfelder, *J. Physical Chem.*, 1934, **38**, 978.

[28] *J.*, 1934, 1144; *A.*, 1068.

[29] Cf. *Ann. Reports*, 1930, **27**, 333.

[30] *Physikal. Z.*, 1932, **33**, 941; 1933, **34**, 593; *A.*, 1933, 8, 908; *Z. Elektrochem.*, 1933, **39**, 517; *A.*, 1933, 908.

[31] *Physikal. Z.*, 1933, **34**, 625; *A.*, 1933, 1015.

[32] *Z. Elektrochem.*, 1933, **39**, 478; *A.*, 1933, 908.

[33] See, *e.g.*, A. Deubner, *Physikal. Z.*, 1932, **33**, 223; *A.*, 1932, 342; M. Wien, *Ann. Physik*, 1931, [v], **11**, 429; *A.*, 1931, 1370; O. Neese, *ibid.*, 1931, [v], **8**, 929; *A.*, 1931, 801; J. Malsch, *Physikal. Z.*, 1932, **33**, 19; *A.*, 1932, 214; *Ann. Physik*, 1932, [v], **12**, 865; *A.*, 1932, 470.

Improvements have also been made in the experimental measurement of conductivities at high field strengths.[37] To avoid undue development of heat, such experiments have to be carried out with discharges of very short duration, so that there is a kind of dispersion effect superimposed upon the field effect, which appears experimentally as a variation of conductivity with duration of discharge.[38] A theoretical treatment of this phenomenon has been given by H. Falkenhagen.[39]

Since the equivalent conductivity in very high fields approaches the value it has at infinite dilution,[40] it has been suggested that such experiments might be used to determine the true ionic concentration of electrolyte solutions. Matters are, however, complicated by the discovery that weak electrolytes give an abnormally great increase of conductivity at high field strengths.[41] This can only be attributed to an actual increase in the number of ions present, *i.e.*, a displacement of the dissociation equilibrium by the tendency of the field to split up the undissociated molecules. This effect has been termed the dissociation field effect, and has been treated theoretically by L. Onsager,[42] who obtains the equation

$$K_E/K_0 = 1 + Ee_1e_2\,(e_1l_1 + e_2l_2)/D_0k^2T^2(l_1 + l_2) \quad . \quad (6)$$

where K_E is the dissociation constant in a field E, and the ions have charges e_1 and e_2 and mobilities l_1 and l_2. Both the nature and the observed order of magnitude of this effect agree with this expression.

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[34] M. Wien and O. Neese, *loc. cit.*, ref. (33); W. Orthmann, *Ann. Physik*, 1931, [v], **9**, 537; *A.*, 1931, 786; E. Plötze, *ibid.*, 1933, [v], **18**, 288; *A.*, 1933, 1243; H. Geest, *Physikal. Z.*, 1933, **34**, 660; *A.*, 1933, 1015.

[35] M. Jezewski and J. Kamecki, *ibid.*, pp. 88, 561; *A.*, 1933, 250, 901; E. Glowatski, *Ann. Physik*, 1933, [v], **18**, 217; *A.*, 1933, 1120.

[36] B. G. Whitmore, *Physikal. Z.*, 1933, **34**, 649; *A.*, 1933, 1015.

[37] M. Wien, *ibid.*, 1931, **32**, 545; *A.*, 1931, 1012; F. Bauer, *Ann. Physik*, 1930, [v], **6**, 253; *A.*, 1930, 1254; W. Fucks, *ibid.*, **12**, 306; *A.*, 1932, 231.

[38] See M. Wien, *loc. cit.*, ref. (37).

[39] *Physikal. Z.*, 1931, **32**, 353; *A.*, 1931, 686.

[40] Cf. *Ann. Reports*, 1930, **27**, 334.

[41] M. Wien, *loc. cit.*, ref. (37); J. Schiele, *Ann. Physik*, 1932, [v], **7**, 811; *A.*, 1932, 813; *Physikal. Z.*, 1933, **34**, 60; *A.*, 1933, 231.

[42] *J. Chem. Physics*, 1934, **2**, 599; *A.*, 1176.

L. Onsager and N. N. T. Samaras [43] have also extended the number of applications of the electrostatic picture by deducing an expression for the surface tension of dilute electrolyte solutions. They obtain a limiting law of the form

$$\sigma = \sigma_0 + Ac \log (B/c) \quad . \quad . \quad . \quad . \quad (7)$$

where A and B are constants depending only on the valency type of the salt and the nature of the solvent. The available experimental data [44] are not sufficiently accurate to test this relation strictly, but the change of surface tension is roughly the same for all uni-univalent salts, and the results are not incompatible with equation (6).

We have so far dealt only with the limiting laws for conductivity, etc., which are theoretically valid only at infinite dilution. Other factors must be introduced to account for the behaviour of aqueous solutions of higher concentrations, and in non-aqueous solutions it is rarely possible to reach dilutions at which the limiting laws are obeyed.[45] There are, in principle, two possible lines of approach in treating more concentrated solutions; one is to obtain a more accurate mathematical treatment of the electrostatic model, and the other to allow for the existence of undissociated molecules in solution. The principles involved in these two methods of treatment have been recently dealt with; [46] in the case of non-stationary phenomena, however, the second alternative provides the only possibility of quantitative treatment, since it has so far only been possible to obtain the first approximation (corresponding to the limiting law) in solving the differential equations involved. O. Redlich [47] has obtained an equation for conductivity corresponding to the second approximation of Debye and Hückel for activity coefficients, and finds agreement up to $0{\cdot}1N$ for the alkali halides, but unfortunately his treatment refers to the incorrect equations of Debye and Hückel, which do not take into account the Brownian movement. It is probable, however, that an analogous treatment of the correct Onsager equations would lead qualitatively to similar results, *i.e.*, to a conductivity curve lying above the limiting straight line. In many cases the deviation is actually in the opposite direction, and although it is possible that higher degrees of approximation would reproduce this feature (as in the case of activity coefficients),[48] the only quantitative treatment possible at present is to attribute all deviations from equation (2) to incomplete dissociation. Methods hitherto employed for the quantitative treatment of conductivity data have made use of the limiting law for the activity coefficients of the ions, and have assumed a value for Λ_0. R. M. Fuoss and C. A. Kraus [49] have recently devised a valuable method of computation (employing the second approximation of Debye and Hückel for the activity coefficients) [50] in which both Λ_0 and the degree of dissociation are derived from the experimental data by a series of successive approximations. They have applied this method with success to a number of widely differing examples, the dielectric constants varying from 2 to 80, and the values of the dissociation constant from 0·17 to 0·00007. The same authors [51] have accounted quantitatively for the appearance of minima in solvents of low dielectric constant by assuming the formation of ion triplets capable of carrying current, which are in equilibrium with ions and neutral molecules.[51] The theory agrees well with the results for tetra*iso*amylammonium nitrate in dioxan–water mixtures with dielectric constants lower than 10.[52]

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[43] *J. Chem. Physics*, 1934, **2**, 528. Cf. also C. Wagner, *Physikal. Z.*, 1924, **25**, 474; *A.*, 1925, ii, 387.

[44] See, *e.g.*, A. Schwenker, *Ann. Physik*, 1931, **11**, 525; *A.*, 1931, 366.

[45] In this connexion, it may be noted that J. E. Coates and E. G. Taylor (*Nature*, 1934, **134**, 141; *A.*, 967) have found that the Onsager equation is obeyed by a number of salts in liquid hydrogen cyanide (dielectric constant about 95) over the concentration range $0{\cdot}0001$—$0{\cdot}005N$.

[46] *Ann. Reports*, 1932, **29**, 21; 1933, **30**, 22.

[47] *Physikal. Z.*, 1925, **26**, 199; 1926, **27**, 528; *A.*, 1925, ii, 541; 1926, 910.

The nature of the forces involved in the formation of the undissociated molecules still remains a fairly open question. If these are purely electrostatic (as in Bjerrum's conception of ionic association), the dissociation constants obtained should be a unique function of the dielectric constant of the solvent and a parameter a representing the distance of closest approach of the ions. This is found to be the case for the same solutions, where the variation of dissociation constant with dielectric constant can be accounted for quantitatively by assuming a reasonable constant value for a.[53] The formation of triple ions can also be treated by assuming only electrostatic forces to be operative, and the expressions obtained agree fairly well with the conductivity minima observed for salts in dioxan–water mixtures and in benzene.[52] It is interesting to note that the theory approximately reproduces the relation $c_{\text{min.}} = \text{const.} \times D^3$ (where $c_{\text{min.}}$ is the concentration corresponding to the minimum in the conductivity curve), previously advanced empirically by Walden. However, this simple picture is only valid in a very limited number of cases, and, on account of solvation, the degree of dissociation of an electrolyte depends, in general, not only on the dielectric constant of the solvent, but also on its chemical type. Moreover, in the case of many electrolytes (*e.g.*, weak acids and bases and certain salts such as those of thallium and lead), the formation of an undissociated molecule involves specific chemical forces. These factors were dealt with in a recent report,[54] and we need only point out here that recent work in a number of widely differing solvents continues to emphasise the diversity of electrochemical behaviour, *e.g.*, in acetone, methyl ethyl ketone,[55] acetophenone, *cyclo*hexanone,[56] cyanoacetic ester, *o*-cyanotoluene,[57] aniline,[58] anhydrous hydrazine,[59] nitromethane,[60] nitrobenzene,[61] liquid ammonia,[62] and metallic alkyls.[63] H. Ulich [64] has published a discussion of the extreme types of physical and chemical interaction encountered. It is interesting to note that a suitable type of solvent may cause ionisation with solutes usually considered to be non-electrolytes, *e.g.*, iodine and cyanogen iodide give conducting solutions in pyridine and ketones, both I^+ and I^- being apparently formed,[65] while aromatic nitro-compounds in anhydrous hydrazine are said to ionise according to the scheme $ArNO_2 + N_2H_4 \rightleftharpoons ArNO_2^+ + N_2H_4^-$, only an electron transfer being involved.[66]

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[48] See *Ann. Reports*, 1932, **29**, 24. The development of such "higher terms" is in any case open to theoretical criticism; see *ibid.*, 1933, **30**, 22.

[49] *J. Amer. Chem. Soc.*, 1933, **55**, 476; *A.*, 1933, 353.

[50] The ionic radius occurring in this expression was calculated from the mobilities by applying Stokes's law.

[51] *Ibid.*, p. 2387; *A.*, 1933, 785.

[52] *Idem*, *ibid.*, p. 26.

[53] *Idem*, *ibid.*, p. 1019; *A.*, 1933, 464. A refinement of Bjerrum's treatment has been given by Fuoss, *Trans. Faraday Soc.*, 1934, **30**, 967; *A.*, 1173.

It would be very valuable to have some independent evidence of the degree of solvation and association and the nature of the forces involved in these processes, especially in more concentrated solutions where the above methods of treatment lose their validity.

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[54] *Ann. Reports*, 1930, **27**, 326.

[55] P. Walden and E. J. Birr, *Z. physikal. Chem.*, 1931, **153**, 1; *A.*, 1931, 434.

[56] *Idem, ibid.*, 1933, **165**, 26, 32; *A.*, 1933, 784.

[57] J. C. Philip and P. Rangaramanujam, *J.*, 1932, 1512; *A.*, 1932, 699.

[58] P. Walden and L. F. Audrieth, *Z. physikal. Chem.*, 1933, **165**, 11; *A.*, 1933, 784.

[59] P. Walden and H. Hilgert, *ibid.*, p. 907; *A.*, 1933.

[60] Walden and Birr, *ibid.*, **162**, 263; *A.*, 1933, 467.

[61] W. F. K. Wynne-Jones, *J.*, 1931, 795; *A.*, 1931, 686. See also ref. (60).

[62] C. A. Kraus and W. W. Hawes, *J. Amer. Chem. Soc.*, 1933, **55**, 2776; *A.*, 1933, 907.

[63] F. Hein and H. Pauling, *Z. physikal. Chem.*, 1933, **165**, 38; *A.*, 1933, 907; *Z. Elektrochem.*, 1933, **39**, 537; *A.*, 1933, 907.

[64] *Ibid.*, p. 483; *A.*, 1933, 908.

[65] L. F. Audrieth and E. J. Birr, *J. Amer. Chem. Soc.*, 1933, **55**, 668; *A.*, 1933, 354; E. J. Birr, *Z. physikal. Chem.*, 1933, **165**, 311; *A.*, 1933, 907.

[66] P. Walden, *Z. physikal. Chem.*, 1934, **168**, 419; *A.*, 845.

Such evidence is, however, still very meagre,[67] although interesting work has recently been done by H. Fromherz and his collaborators [68] on the ultra-violet absorption spectra of aqueous solutions of metallic halides. They find that for the alkali and alkaline-earth halides the changes of absorption spectra with concentration are of the type expected for a purely electrostatic association, while for the halides of lead and thallium frequencies appear corresponding to a much more permanent and intimate combination.

It has been pointed out by P. Debye [69] that, although the masses of the ions play no part in determining most of the properties of ionic solutions, they are of importance in the propagation of a supersonic wave through an electrolyte. By measuring the differences in potential set up, Debye proposes to measure the masses of the ions, so that the method may prove valuable in obtaining information about solvation. It should be noted that the recent extension of measurements with the ultra-centrifuge to inorganic salts [70] does not give any direct information about solvation, since attachment of solvent by the ion will only affect the results in so far as it alters the volume of the solution. R. P. B.

7. KINETIC SALT EFFECTS.

The chief contribution made by the interionic theory to reaction kinetics has been by means of the equation first given by J. N. Brönsted in 1922,[1] according to which the velocity of a reaction between A and B is given by

$$v = kc_Ac_Bf_Af_B/f_X \quad \ldots\ldots \quad (1)$$

where the f's are activity coefficients and X is an intermediate "critical complex." The exact nature of X is somewhat indeterminate, so that the value of f_X is in general unknown. In the case of reactions between ions, however, the electrostatic charge of X must always be the algebraic sum of the charges on A and B, and this makes it possible to predict the variation of the factor f_Af_B/f_X with salt concentration. It is well known that these predictions as to the sign and magnitude of the salt effect for ionic reactions have been amply verified, and it is therefore surprising to find that there is still considerable difference of opinion as to the theoretical interpretation of equation (1). Brönsted's original derivation[2] assumed that the rate-determining process was the formation of X from A and B, and justified the form of the equation by rather arbitrary considerations. A more generally accepted view is that of N. Bjerrum,[3] according to which the term $c_A c_B f_A f_B / f_X$ represents the concentration of a complex in equilibrium with A and B, and the velocity-determining stage is the decomposition of X at a rate proportional to its concentration.

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[67] Cf. *Ann. Reports*, 1932, **29**, 22.

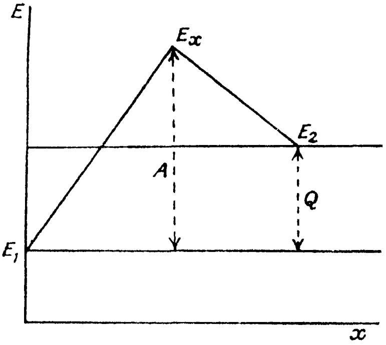
[68] H. Fromherz and W. Menschick, *Z. physikal. Chem.*, 1930, [*B*], **7**, 439; *A.*, 1930, 853; H. Diamond and Fromherz, *ibid.*, 1930, [*B*], **9**, 289; *A.*, 1930, 1234; Fromherz and Kun-Hou-Lih, *ibid.*, 1931, [*A*], **153**, 321; *A.*, 1931, 565.

[69] *J. Chem. Physics*, 1933, **1**, 13; *A.*, 1933, 348. Cf. also S. Oka, *Proc. Phys.-Math. Soc. Japan*, 1933, **15**, 413; *A.*, 354.

[70] K. O. Pedersen, *Z. physikal. Chem.*, 1934, **170**, 41.

[1] Cf. *Ann. Reports*, 1926, **23**, 30—37; 1927, **24**, 330—335.

An interpretation of equation (1) in terms of modern views on reaction kinetics has been put forward by V. K. LaMer.[4] According to these views, the change in potential energy during an " adiabatic " reaction[5] may be represented schematically by the figure, where the co-ordinate x represents some distance which changes during the course of the reaction, Q is the energy change during the reaction, and A the energy of activation. LaMer identifies the critical complex of Brönsted's theory with the state of maximum potential energy (E_X) during the reaction. E_1 is the potential energy of the initial state, and for a reaction between A and B can be written as $E_A + E_B$. If the medium is now altered, *e.g.*, by adding salt, E_A, E_B, and E_X will each be changed, and the resulting change in the heat of activation is given by



$$\Delta A = \Delta E_X - \Delta E_A - \Delta E_B \quad . \quad . \quad . \quad . \quad (2)$$

Further, the reaction velocity v is related to the heat of activation by an equation of the form

$$v = PZ\, e^{-A/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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[2] *Z. physikal. Chem.*, 1922, **102**, 169; 1925, **115**, 337; *A.*, 1922, ii, 699; 1925, ii, 681.

[3] *Ibid.*, 1924, **108**, 82; 1925, **118**, 251; *A.*, 1924, ii, 240; 1925, ii, 131.

[4] *Chem. Reviews*, 1932, **10**, 192.

[5] Cf. *Ann. Reports*, 1930, **27**, 19.

where Z is a collision factor proportional to $c_A c_B$, and P is a phase factor which involves *inter alia* the relative orientations of the molecules. If therefore it is assumed that P and Z are unaffected by the addition of salt, the velocity is given by

$$\log v/v_0 = -\Delta A/RT = \Delta E_A/RT + \Delta E_B/RT - \Delta E_X/RT \quad (4)$$

where v_0 is the velocity in absence of salt. Moreover, if the original medium is taken as the standard state, the activity coefficients in presence of salt are given by $\log f_A = \Delta E_A/RT$, etc., giving $v/v_0 = f_A f_B/f_X$, which is identical with Brönsted's formula. It should be noticed that this treatment does not necessarily assume that all systems reaching the state X will react, but only that the fraction doing so is not affected by the change in the medium. If this fraction is nearly unity, LaMer's treatment is equivalent to Brönsted's original derivation, while if it is very small, Bjerrum's hypothesis will be valid. The changes in heat of activation demanded by the theory are too small to be detected experimentally with certainty.

If the Debye–Hückel limiting law is employed for the activity coefficients of A, B, and X, and the numerical values of the constants for water at 20° inserted, equation (1) gives

$$\log v/v_0 = z_A z_B \sqrt{\mu} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where z_A and z_B are the valencies of A and B and μ is the ionic strength. As previously indicated,[1] this equation has received considerable experimental support, and further work confirms its validity as a limiting law in dilute solution.[6] Outside the range of extremely dilute solution it is impossible, in general, to predict the dependence of the factor $f_A f_B/f_X$ upon salt concentration, and there is obviously no method of arriving at this experimentally. It has, however, been found that when multiply-charged ions of opposite sign are present simultaneously, the limiting laws for activity coefficients fail even at the lowest concentrations hitherto measured,[7] and it is of interest to inquire whether the kinetic salt effect exhibits similar behaviour. A very suitable reaction for the purpose is

$$CH_2Br{\cdot}CO_2' + S_2O_3'' \longrightarrow [X]''' \longrightarrow CH_2(S_2O_3'){\cdot}CO_2' + Br'$$

where the critical complex has a triple charge. Unfortunately, the experimental evidence is at present very discordant. Both LaMer and Kappanna[6] agree that equation (5) is obeyed in presence of univalent cations, and von Kiss [8] and A. N. Kappanna and H. W. Patwardhan [9] find independently that this is also the case in the presence of magnesium and calcium ions. LaMer and R. W. Fessenden,[10] on the other hand, find large deviations from the limiting law in the latter case, and obtain curves which resemble the solubility curves of uni-tervalent cobaltammines in salt solutions containing bivalent cations.[11] Further information on this point would be of great interest for the fundamental theory of equation (1). It may be noted in this connexion that LaMer has shown [12] that if more than one energy state contributes to the critical configuration, then f_X cannot be strictly interpreted as a thermodynamic activity coefficient.

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[6] *E.g.*, V. K. LaMer, *J. Amer. Chem. Soc.*, 1929, **51**, 334; *A.*, 1930, 168; A. N. Kappanna, *J. Indian Chem. Soc.*, 1929, **6**, 45; *A.*, 1929, 516; A. von Kiss and I. Bossanyi, *Z. anorg. Chem.*, 1930, **191**, 289; 1931, **198**, 102; 1932, **206**, 196; *A.*, 1930, 1256; 1931, 802; 1932, 702.

[7] This behaviour can be accounted for by the principle of specific interaction; cf. *Ann. Reports*, 1933, **30**, 24.

LaMer and M. E. Kamner [13] have studied the reaction between β-bromopropionate and thiosulphate ions, and find a salt effect in the opposite sense to that predicted by equation (5). It is not surprising that the simple theory should fail in this case, since the seat of the charge is now some distance from the part of the molecule which reacts. LaMer and Kamner account for the negative salt effect by assuming that in the absence of salt the molecules reacting automatically orient themselves in the most favourable way, while the presence of other ions sets up a rapidly fluctuating field which disturbs this orientation. This effect [corresponding to a change of P in equation (3)] must be assumed to be negligible in reactions which obey the Brönsted formula. M. H. Bedford, R. B. Mason, and C. E. Morrell,[14] studying the reactions between the thiosulphate ion and the ions of brominated malonic and succinic acids, have also found a negative salt effect which they attribute to decreased orientation. The supposed failure of the Brönsted equation in other cases [15] is probably due to its application to solutions not sufficiently dilute to obey the limiting laws.[16]

All the above considerations apply to reactions involving strong electrolytes, and the effects observed are termed *primary salt effects.* If, however, the reactions involve incompletely dissociated electrolytes, the effect of added salt on the activity coefficients of the ions

[8] A. von Kiss and P. Vass, *Z. anorg. Chem.*, 1934, **217**, 305; *A.*, 603.

[9] *Rec. trav. chim.*, 1932, **51**, 379; *A.*, 1932, 1210.

[10] *J. Amer. Chem. Soc.*, 1932, **54**, 2351; *A.*, 1932, 815.

[11] Cf. V. K. LaMer and C. F. Mason, *ibid.*, 1927, **49**, 363, 410; *A.*, 1927, 314; LaMer and R. G. Cook, *ibid.*, 1929, **51**, 2622; *A.*, 1929, 1386; LaMer and F. H. Goldman, *ibid.*, 1929, **51**, 2632; *A.*, 1929, 1387.

[12] *J. Chem. Physics*, 1933, **1**, 289.

[13] *J. Amer. Chem. Soc.*, 1931, **53**, 2832; *A.*, 1931, 1132.

[14] *Ibid.*, 1934, **56**, 280; *A.*, 369.

[15] V. K. LaMer and J. Greenspan, *ibid.*, p. 1492; *A.*, 651.

[16] M. Kilpatrick, *ibid.*, p. 2326.

will displace the dissociation equilibrium and hence alter the actual concentrations of the reacting ions present. The change in reaction velocity thus caused is termed a *secondary salt effect*, and is of particular interest in the study of catalysis by weak acids or weak bases.[17] Many examples of the distinction between the primary and secondary effects are given by J. N. Brönsted.[18]

In principle, there is no reason why equation (1) should be restricted to reactions between ions. In practice, however, no general predictions can be made about f_X for reactions between an ion and a neutral molecule or between two neutral molecules, although some attempts have been made in this direction.[19]

R. P. B.

8. ACIDS AND BASES.

The classical conceptions of acids and bases have undergone great changes in the last ten years or so, and the new ideas have now become so generally accepted that a general review of recent developments in the subject may be of interest. For many years acids and bases were defined as substances giving rise respectively to hydrogen ions and hydroxyl ions in aqueous solution. This definition could be extended without much difficulty to other hydroxylic solvents by substituting, *e.g.* the ethoxide ion for the hydroxyl ion, and the position was rendered more symmetrical by the gradual realisation [1] that the "hydrogen ion" is never simply a proton $H^{\cdot}$, but exists entirely in water as $H_3O^{\cdot}$, in alcohol as $C_2H_5{\cdot}OH_2^{\cdot}$, etc. Such ideas, however, admit the existence of acid and basic attributes only in the presence of a suitable solvent, and such a reaction as the combination of ammonia and hydrogen chloride in the gas phase or in benzene solution would not be classed as an acid–base reaction. The inadequacy of such a point of view appears still more clearly when it is realised that benzene solutions of acids and bases exhibit such typical behaviour as indicator reactions [2] and electrometric titration,[3] although there are no hydrogen ions present, and no possibility for the existence of hydroxyl ions or their analogues.

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[17] See this Report, p. 72.

[18] *Chem. Reviews*, 1928, **5**, 265; *Trans. Faraday Soc.*, 1928, **24**, 630.

[19] G. Scatchard, *Chem. Reviews*, 1932, **10**, 236; H. Harned and N. N. T. Samaras *J. Amer. Chem. Soc.*, 1932, **54**, 9; *A.*, 1932, 346; Samaras, *J. Physical Chem.*, 1933, **37**, 437.

[1] See, *e.g.*, H. Goldschmidt and O. Udby, *Z. physikal. Chem.*, 1907, **60**, 728; *A.*, 1907, ii, 852; K. Fajans, *Ber. physikal. Ges.*, 1919, **21**, 709; *A.*, 1920, ii, 12; A. Hantzsch, *Z. Elektrochem.*, 1924, **30**, 194; K. Fajans and G. Joos, *Z. Physik*, 1924, **23**, 1; *A.*, 1924, ii, 372; G. Scatchard, *J. Amer. Chem. Soc.*, 1925, **47**, 2098; *A.*, 1925, ii, 971; T. M. Lowry, *J.*, 1925, 1372; *A.*, 1925, i, 886; J. N. Brönsted, *J. Physical Chem.*, 1926, **30**, 777; *A.*, 1926, 797.

[2] J. N. Brönsted, *Ber.*, 1928, **61**, [*B*], 2049; *A.*, 1928, 1188; A. Hantzsch and W. Voigt, *ibid.*, 1929, **62**, [*B*], 970; *A.*, 1929, 666.

The matter was put on a much more logical basis by J. N. Brönsted[4] and T. M. Lowry,[5] who almost simultaneously proposed as a definition that *an acid is any substance having a tendency to lose a proton, and a base is any substance having a tendency to take up a proton.* Acids and bases thus form corresponding pairs, related by equations of the type

$$A \rightleftharpoons B + H^{\cdot} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

such pairs are $CH_3{\cdot}CO_2H$ and $CH_3{\cdot}CO_2'$, $NH_4^{\cdot}$ and NH_3, $H_3O^{\cdot}$ and H_2O, etc. It should be noted that there is no restriction as to the charge on an acidic or basic molecule, but that there is always unit difference of charge between a corresponding pair. This apparently formal definition not only rationalises our general ideas about acids and bases, but by extending the terms acid and base to such species as $NH_4^{\cdot}$ and $CH_3{\cdot}CO_2'$, it has led to important discoveries in connexion with acid and basic catalysis. In particular, it shows that OH' and $H_3O^{\cdot}$ do not occupy any unique position among acids and bases, except in so far as they are formed from the solvent itself.

Since a free proton can never exist in the presence of other molecules, equation (1) does not represent an observable process. The actual acid–base equilibria which we study are obtained by combining two such equations, giving

$$A_1 + B_2 \rightleftharpoons A_2 + B_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

A_1, B_1, and A_2, B_2 being two corresponding acid–base pairs. A special case of this is when one of the acid–base pairs is provided by the solvent, giving, *e.g.*,

$$\underset{\text{acid 1}}{CH_3{\cdot}CO_2H} + \underset{\text{base 2}}{H_2O} \rightleftharpoons \underset{\text{acid 2}}{H_3O^{\cdot}} + \underset{\text{base 1}}{CH_3{\cdot}CO_2'}$$

$$\underset{\text{base 1}}{NH_3} + \underset{\text{acid 2}}{H_2O} \rightleftharpoons \underset{\text{base 2}}{OH'} + \underset{\text{acid 1}}{NH_4^{\cdot}}$$

In this case water can act either as a base or as an acid, the corresponding acid and base being $H_3O^{\cdot}$ and OH'. This point of view has brought into clearer relief the essential part played by the solvent in the dissociation of acids and bases, and greatly simplifies the treatment of problems such as hydrolysis and buffer solutions.

These considerations have also an important bearing on the quantitative definition of acid and basic strength, and as there is considerable confusion about the different constants used we shall outline the position here.[6] The most logical definition would be on the basis of equation (1), *i.e.*,

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[3] V. K. LaMer and H. C. Downes, *J. Amer. Chem. Soc.*, 1931, **53**, 888; *A.*, 1931, 584.

[4] *Rec. trav. chim.*, 1923, **42**, 718.

[5] *Chem. and Ind.*, 1923, **42**, 43; *A.*, 1923, ii, 849.

$$K_{\text{acid}} = a_{\text{H}^{\cdot}} \cdot C_{\text{B}}/C_{\text{A}}\,;\ K_{\text{base}} = C_{\text{A}}/C_{\text{B}}a_{\text{H}^{\cdot}} \quad . \quad . \quad . \quad (3)$$

where the C's are concentrations, and $a_{\text{H}^{\cdot}}$ is the proton activity. These constants are a direct measure of the tendency of the molecules to lose or gain a proton, and may be termed absolute acidity constants. They are, however, of no service in practice, since we cannot measure $a_{\text{H}^{\cdot}}$, and it is probably in principle indefinable.[7] The type of equilibrium actually studied involves two acid–base pairs, and from equation (2) we can define an equilibrium constant by

$$K = C_{\text{A}_2}C_{\text{B}_1}/C_{\text{A}_1}C_{\text{B}_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If one acid–base pair is kept the same, this constant provides a means of comparing the acid or basic strengths of the other pairs involved. The natural standard to use is the solvent, and we may thus define the so-called "rational constants," which for aqueous solutions become

$$K_{\text{A}}\,(\text{rat.}) = C_{\text{B}}C_{\text{H}_3\text{O}^{\cdot}}/C_{\text{A}}C_{\text{H}_2\text{O}}\,;\ K_{\text{B}}\,(\text{rat.}) = C_{\text{A}}C_{\text{OH}'}/C_{\text{B}}C_{\text{H}_2\text{O}} \quad (5)$$

The rational acidity constant may be considered as the ratio of the absolute acidity constant of the acid to that of the solvent, and similarly for the basicity constants. Since the concentration of water is constant, the rational constants are proportional to the conventional dissociation constants, according to the equations

$$\left.\begin{aligned} K_{\text{A}} &= K_{\text{A}}\,(\text{rat.}) \times C_{\text{H}_2\text{O}} = C_{\text{B}}C_{\text{H}_3\text{O}^{\cdot}}/C_{\text{A}} \\ K_{\text{B}} &= K_{\text{B}}\,(\text{rat.}) \times C_{\text{H}_2\text{O}} = C_{\text{A}}C_{\text{OH}'}/C_{\text{B}} \end{aligned}\right\} \quad . \quad . \quad (6)$$

Similar sets of constants can obviously be defined for any other solvent capable of acting both as an acid and a base. The constants in equations (4)—(6) are not true thermodynamic constants, but may be related to them by introducing a term involving activity coefficients, *e.g.*,

$$K'_{\text{A}} = a_{\text{B}}a_{\text{H}_3\text{O}^{\cdot}}/a_{\text{A}} = K_{\text{A}}f_{\text{B}}f_{\text{H}_3\text{O}^{\cdot}}/f_{\text{A}} \quad . \quad . \quad . \quad (7)$$

K'_{A} and K_{A} becoming identical in infinitely dilute solution.

The best methods for measuring dissociation constants are those

[6] The quantitative statement of the problem was first given by Brönsted in a Danish monograph "Om Syre og Basekatalyse" (Copenhagen, 1926), later translated into English (*Chem. Reviews*, 1928, **3**, 231). Other papers by Brönsted are: *Ber.*, 1928, **61**, [*B*], 2049; *A.*, 1928, 1188; *Z. physikal. Chem.*, 1934, **169**, 52; *A.*, 962.

[7] See E. A. Guggenheim, *J. Physical Chem.*, 1930, **34**, 1758; *A.*, 1930, 1124; P. B. Taylor, *ibid.*, 1927, **31**, 1478; *A.*, 1927, 1144.

involving measurement of the concentration of one of the species present. In the case of coloured substances, this may be done very accurately by means of modern colorimetric technique, which has been employed by P. Gross, A. Jamöck, and F. Patat [8] for measuring the dissociation constant of picric acid in ethyl alcohol and by H. von Halban and G. Kortüm [9] for dinitrophenol in aqueous salt solutions. L. P. Hammett, A. Dingwall, and L. Flexser [10] have recently extended the same method to colourless solutions by working in the ultra-violet. The catalytic method was one of the first to be used for measuring hydrogen-ion concentrations, and it has recently been used for accurate measurements on monochloroacetic acid [11] and for measuring dissociation constants in ethyl alcohol.[12] The derivation of accurate dissociation constants from conductivity data is rather more complex, involving the variation of mobility with concentration, but convenient methods of computation have recently been devised.[13] Accurate work of this kind has been done recently by D. A. McInnes [14] and by D. J. G. Ives.[15] Most of the methods based on the *E.M.F.* of cells are not suited for accurate measurements, as they involve indeterminate junction potentials, but Harned has recently devised a method using only concentration cells without liquid junctions, and accurate data have been obtained for a number of acids and bases at different temperatures.[16] It is gratifying to note that the value obtained by McInnes for the thermodynamic dissociation constant of acetic acid at 25° ($1{\cdot}753 \times 10^{-5}$) is almost identical with the value obtained by Harned and Ehlers using an entirely different method ($1{\cdot}754 \times 10^{-5}$).

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[8] *Monatsh.*, 1933, **63**, 117.

[9] *Z. Elektrochem.*, 1934, **40**, 502; *A.*, 962.

[10] *J. Amer. Chem. Soc.*, 1934, **56**, 2010; *A.*, 1173. For a new type of spectrophotometer suitable for such work, see L. A. Woodward, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 118.

[11] C. Grove, *J. Amer. Chem. Soc.*, 1930, **52**, 1404; *A.*, 1930, 698.

[12] A. J. Deyrup, *ibid.*, 1934, **56**, 60; *A.*, 260.

[13] See this Report, p. 65.

[14] *J. Amer. Chem. Soc.*, 1926, **48**, 2068; *A.*, 1926, 906; McInnes and T. Shedlovsky, *ibid.*, 1932, **54**, 1429; *A.*, 1932, 695; cf. also B. Saxton and T. W. Langer, *ibid.*, 1933, **55**, 3638; *A.*, 1933, 1118.

[15] *J.*, 1933, 731; *A.*, 1933, 780.

[16] H. S. Harned and B. B. Owen, *J. Amer. Chem. Soc.*, 1930, **52**, 5079; *A.*, 1931, 308 (acetic and formic acids, aliphatic amines, and glycine at 25°); Harned and R. W. Ehlers, *ibid.*, 1932, **54**, 1350; *A.*, 1932, 695 (acetic acid, 0—35°); *ibid.*, 1933, **55**, 652; *A.*, 1933, 350 (acetic acid, 0—60°); *ibid.*, 1933, **55**, 2379; *A.*, 1933, 780 (propionic acid, 0—60°); B. B. Owen, *ibid.*, 1934, **56**, 24; *A.*, 254 (glycine, 10—45°); *ibid.*, 1934, **56**, 1695; *A.*, 1071 (boric acid, 10—50°); D. A. McInnes and D. Belcher, *ibid.*, 1933, **55**, 2630 (carbonic acid at 25°); Harned and R. O. Sutherland, *ibid.*, 1934, **56**, 2039; *A.*, 1307 (*n*-butyric acid, 0—60°); Harned and N. D. Embree, *ibid.*, 1934, **56**, 1042; *A.*, 731 (formic acid, 0—60°); L. F. Nims, *ibid.*, 1934, **56**, 1110; *A.*, 731 (phosphoric acid, 0—40°); D. D. Wright, *ibid.*, 1934, **56**, 314; *A.*, 364 (monochloroacetic acid, 0—40°).

Instead of measuring directly the equilibrium with the solvent, it is often convenient to add a third acid–base system having coloured components, *i.e.*, an indicator. If, then, the equilibrium constant between the indicator and the solvent is known, measurements of the concentrations of the two forms of the indicator present will give the position of the equilibrium between the first acid–base system and the solvent. The method has, of course, been thoroughly worked out for aqueous solutions,[17] but considerable care is necessary in transferring the method to other solvents without independent investigation, as it has been found in some cases that the absorption spectrum of the indicator varies considerably with the nature of the solvent [18] and that the colour change may even take place in different stages in different solvents.[19]

Since at least two of the activity coefficients in equation (7) refer to ions, the Debye–Hückel theory may be used to predict the variation of the dissociation constant with ionic strength. If, in the equilibrium $A + H_2O \rightleftharpoons B + H_3O^{\cdot}$, the (positive) valency of A is z, the limiting law for water at 20° is easily shown to be

$$\log_{10} K_A = \log_{10} K'_A - (z - 1)\sqrt{\mu} \quad . \quad . \quad . \quad (8)$$

where μ is the ionic strength. The case $z = 0$ corresponds to the dissociation of an ordinary uncharged acid, and the corresponding increase of dissociation constant with increasing ionic concentration is amply confirmed by the accurate measurements quoted above.[20] For equilibrium between ammonia and the ammonium ion (or the analogous case of an amine), $z = 1$, and as predicted by the equation there is very little change of dissociation constant with salt concentration in dilute solution. Brönsted [21] has made an interesting experimental study of equilibria of the type

$$[Cr(H_2O)_6]^{\cdot\cdot\cdot} + H_2O \rightleftharpoons \left[Cr{(OH) \atop (H_2O)_5}\right]^{\cdot\cdot} + H_3O^{\cdot}$$

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[17] For recent work, see, *e.g.*, N. V. Sidgwick, W. J. Worboys, and L. A. Woodward, *Proc. Roy. Soc.*, 1930, **129**, [*A*], 527; *A.*, 1931, 39; Sidgwick and Woodward, *ibid.*, 1930, **130**, 1; *A.*, 1931, 168; E. A. Guggenheim and F. D. Schlinder, *J. Physical Chem.*, 1934, **38**, 543.

[18] H. Baggesgaard-Rasmussen and F. Reimers, *Dansk Tidsskr. Farm.*, 1933, **7**, 225; *A.*, 1934, 160.

[19] See, *e.g.*, J. N. Brönsted, A. Delbanco, and A. Tovborg-Jensen, *Z. physikal. Chem.*, 1934, **169**, 361; *A.*, 1070.

[20] See especially McInnes and Shedlovsky, *loc. cit.*, ref. (14); Shedlovsky, A. S. Brown, and D. A. McInnes, *Trans. Amer. Electrochem. Soc.*, 1934, **66**, 237; *A.*, 1308.

[21] J. N. Brönsted and C. V. King, *Z. physikal. Chem.*, 1927, Cohen-Festband, 699; *A.*, 1927, 204; Brönsted and K. Volqvartz, *ibid.*, 1928, **134**, 97; *A.*, 1928, 1326.

corresponding to $z = 3$, and finds the expected large decrease of dissociation constant with increasing ionic concentration.

There have been a number of attempts to employ equation (3) for defining an absolute scale of acidity by means of which acids in different solvents can be compared,[22] but it seems probable that all such definitions must be at best completely arbitrary, since they involve such difficultly accessible concepts as individual ionic activities and potential differences between two phases.[7] It is, however, possible to obtain much interesting information by comparing the rational or conventional dissociation constants in different media, and to obtain a semi-quantitative interpretation of the results. It is now generally realised that the acidic or basic character of the solvent is by far the most important factor affecting the behaviour of dissolved acids or bases. Water and other hydroxylic solvents have been termed by Brönsted "amphiprotic," since they are able either to receive or to lose a proton, and thus act as strongly dissociating media for both acids and bases. Recently, a great deal of interesting work has been done with very acid solvents, *i.e.*, solvents which readily lose a proton but accept one only with difficulty. As long ago as 1908, A. Hantzsch [23] showed by cryoscopic investigations in sulphuric acid that nearly all oxygen compounds can act as bases provided they be dissolved in a medium of sufficient acidity, but it is only recently that quantitative measurements have been carried out in this type of solvent. Conant and his collaborators [24] have carried out electrometric and indicator studies of a large number of acids and bases in anhydrous acetic acid, and conductivity work in the same solvent has been carried out by a number of authors.[25] Two interesting points emerge: in the first place, all bases which in water are stronger than aniline give identical titration curves in acetic acid, and may be considered as strong bases. It is not correct to describe them as completely dissociated, since the low dielectric constant of the solvent will favour considerable ion-pair formation, but the "protolytic" reaction, *e.g.*, $CH_3{\cdot}NH_2 + CH_3{\cdot}CO_2H \longrightarrow [CH_3{\cdot}NH_3]^{\cdot} [CH_3{\cdot}CO_2]'$, has taken place completely. In the second place, a number of acids which in water are completely dissociated (*e.g.*, hydrochloric, perchloric, sulphuric, and benzenesulphonic) give widely differing titration curves in acetic acid. The conductivity measurements are more difficult to interpret owing to the strong interionic forces, but they support the differences between the "strong" acids. Similar results have been obtained with anhydrous formic acid as a solvent by Hammett,[26] who in particular has discovered a large number of indicators suitable for use in such solvents. A medium of continuously varying acidity can be made by mixing sulphuric acid and water in varying proportions, and although the strong buffer action in such a mixture makes electrometric and conductivity measurements useless, Hammett and Deyrup[27] have studied a large number of bases colorimetrically in this solvent, ranging from *p*-nitroaniline, which is appreciably ionised in water, to trinitroaniline, which is incompletely ionised even in concentrated sulphuric acid. Hammett has also investigated a number of indicators in the same solvent,[28] and both he[29] and J. W. Baker[30] have shown how solubility and partition methods may be used for studying basic properties. Many compounds exhibiting hardly any basic properties in water (*e.g.*, esters, ketones, oximes, amides) are strong enough bases in these solvents to permit of quantitative titration, a fact which may prove of practical importance.

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[22] J. N. Brönsted, *Z. physikal. Chem.*, 1929, **143**, 301; *A.*, 1929, 1240; Brönsted, A. Dolbanco, and K. Volqvartz, *ibid.*, 1932, **162**, 128; *A.*, 1933, 26; L. P. Hammett, *J. Amer. Chem. Soc.*, 1928, **50**, 2666; *A.*, 1928, 1325; G. Schwarzenbach, *Helv. Chim. Acta*, 1930, **13**, 870; *A.*, 1930, 1526.

[23] *Z. physikal. Chem.*, 1908, **61**, 257; **65**, 41; *A.*, 1908, ii, 14, 462.

[24] J. B. Conant and N. F. Hall, *J. Amer. Chem. Soc.*, 1927, **49**, 3062; *A.*, 1928, 129; Hall and Conant, *ibid.*, 1927, **49**, 3047; *A.*, 1928, 129; Conant and G. M. Brammann, *ibid.*, 1928, **50**, 2305; *A.*, 1928, 1101; Hall and T. H. Werner, *ibid.*, 1928, **50**, 2367; *A.*, 1928, 1118; Conant and Werner, *ibid.*, 1930, **52**, 4436; *A.*, 1931, 40.

[25] A. Hantzsch and W. Langbein, *Z. anorg. Chem.*, 1932, **204**, 193; *A.*, 1932, 467; F. G. Hall and H. H. Voge, *J. Amer. Chem. Soc.*, 1933, **55**, 239; *A.*, 1933, 230; W. C. Eichelberger and V. K. LaMer, *ibid.*, 1933, **55**, 3635; *A.*, 1933, 1121; I. M. Kolthoff and A. Willan, *ibid.*, 1934, **56**, 1007; *A.*, 735; B. V. Weidner, A. W. Hutchinson, and G. C. Chandlee, *ibid.*, 1934, **56**, 1285; *A.*, 845.

Next to the acidic or basic character of the media involved, the most important factor governing the change of dissociation constant with change of medium is the electrostatic energy of the ions. This appears most clearly by considering the two typical pairs of dissociation equilibria,

$$a \begin{cases} NH_4^{\cdot} + H_2O \rightleftharpoons NH_3 + H_3O^{\cdot} \\ NH_4^{\cdot} + CH_3{\cdot}OH \rightleftharpoons NH_3 + CH_3{\cdot}OH_2^{\cdot} \end{cases}$$

$$b \begin{cases} CH_3{\cdot}CO_2H + H_2O \rightleftharpoons CH_3{\cdot}CO_2' + H_3O^{\cdot} \\ CH_3{\cdot}CO_2H + CH_3{\cdot}OH \rightleftharpoons CH_3{\cdot}CO_2' + CH_3{\cdot}OH_2^{\cdot} \end{cases}$$

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[26] L. P. Hammett and N. Dietz, *J. Amer. Chem. Soc.*, 1930, **52**, 4795; *A.*, 1931, 312; Hammett and A. J. Deyrup, *ibid.*, 1932, **54**, 4239; *A.*, 1933, 26.

[27] *Ibid.*, 1932, **54**, 2721; *A.*, 1933, 26.

[28] L. P. Hammett and M. A. Paul, *ibid.*, 1934, **56**, 827; *A.*, 618.

[29] L. P. Hammett and R. P. Chapman, *ibid.*, p. 1282; *A.*, 839.

[30] *J.*, 1931, 307; *A.*, 1931, 485; *J.*, 1932, 1226; *A.*, 1932, 612; Baker and L. Hey, *ibid.*, p. 2917; *A.*, 1933, 159.

In going from water to methyl alcohol, the effect of the changed solvation of the proton is the same for (*a*) as for (*b*), but the effect of the change of electrostatic energy is obviously much greater for (*b*). Correspondingly, it is found that the dissociation constant of acetic acid decreases by a factor of about 10^4 in passing from water to methyl alcohol, while that of the ammonium ion decreases only by a factor of about 10^2. This was first pointed out by N. Bjerrum and E. Larsson[31] and by Brönsted[32] and is supported by a large amount of evidence.[33] This principle has recently been applied to a study of some amino-acids, where the shift in the titration curve in going from water to alcohol can be used to establish whether or not the amino-acid is present as a " zwitterion."[34]

There is a considerable amount of evidence to show that the ratio of the dissociation constants in two media is approximately the same for all acids of the same charge type,[35] but closer examination shows that this is only true to within a power of ten; this is well shown by the work of J. O. Halford on alcoholic solutions,[36] of M. and M. L. Kilpatrick in the weakly basic solvent acetonitrile,[37] and of Brönsted in the acid solvent *m*-cresol.[38] The available data have been reviewed by W. F. K. Wynne-Jones,[39] who has shown that from a theoretical point of view the individual deviations are due to differences between the transfer energies of the individual acid or base molecules (or ions) within each class. These differences will be small for a series such as the aliphatic carboxylic acids, but may be considerable when comparing *e.g.*, ions of the phenoxide and the carboxylate type. Wynne-Jones has deduced on the basis of electrostatic theory a quantitative relationship between the relative dissociation constants in different solvents, on the assumption that the radii of the ions (excluding the solvated proton) remain constant, and that the non-electrostatic transfer energies are negligible. His equation agrees with the scanty data available for water and the alcohols. As a basis for comparing different acids or bases (*e.g.*, for investigating the relationship between constitution and acid or basic strength) he suggested the use of the "intrinsic strength," obtained by extrapolating the results for different solvents to a hypothetical solvent of infinite dielectric constant, thus eliminating purely electrostatic effects.[40] Since water has such a high dielectric constant, this extrapolation can be easily carried out from the results in water and the alcohols.

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[31] *Z. physikal. Chem.*, 1927, **127**, 358; *A.*, 1927, 928.

[32] *J. Physical Chem.*, 1926, **30**, 777; *A.*, 1926, 797.

[33] See, *e.g.*, L. Michaelis and M. Mizutani, *Z. physikal. Chem.*, 1925, **116**, 135; *A.*, 1925, ii, 793; Mizutani, *ibid.*, 1925, **116**, 318, 350; *A.*, 1925, ii, 867; *ibid.*, 1925, **118**, 327; *A.*, 1926, 125; L. D. Goodhue and R. M. Hixon, *J. Amer. Chem. Soc.*, 1934, **56**, 1329; *A.*, 735.

[34] See, *e.g.*, T. H. Jukes and C. L. A. Schmidt, *J. Biol. Chem.*, 1934, **105**, 359; *A.*, 732; J. T. Edwall and M. H. Blanchard, *J. Amer. Chem. Soc.*, 1933, **55**, 2337; *A.*, 1933, 781.

[35] Bjerrum and Larsson, *loc. cit.*, ref. (31); H. Goldschmidt, C. Görbitz, H. Hongen, and K. Pahle, *Z. physikal. Chem.*, 1921, **99**, 116; *A.*, 1922, ii, 135; W. L. Bright and H. T. Briscoe, *J. Physical Chem.*, 1933, **37**, 787; *A.*, 1933, 904.

[36] *J. Amer. Chem. Soc.*, 1933, **55**, 2272; *A.*, 1933, 780.

[37] *Chem. Reviews*, 1933, **13**, 131.

[38] J. N. Brönsted, A. Delbanco, and A. Tovborg-Jensen, *Z. physikal. Chem.*, 1934, **169**, 52; *A.*, 962.

[39] *Proc. Roy. Soc.*, 1933, [*A*], **140**, 440; *A.*, 1933, 675.

Considerable interest attaches to the behaviour of acids and bases in solvents such as benzene (termed by Brönsted "aprotic" solvents), which possess neither acid nor basic properties. Since the solvent can take no part in a protolytic equilibrium, it is always necessary to add a second acid or base before any measurements can be carried out. By a suitable choice of this auxiliary acid or base, any desired range of acid or basic strength can be studied, whereas in solvents which themselves possess acid or basic properties, this range is limited. Thus, in water, all acids considerably stronger than $H_3O^{\bullet}$ or bases considerably stronger than OH' will be completely dissociated, and will therefore appear to be equally strong. (This property of water and the other hydroxylic solvents has been termed "nivellierend" by Hantzsch.) A scale of acidity in an aprotic solvent is most conveniently constructed by the use of indicators, and this has been done for benzene by Brönsted[41] and by V. K. LaMer and H. C. Downes,[42] and in chloroform by A. Hantzsch and W. Voigt.[43] It has also been found possible to carry out electrometric titrations in this type of solvent.[44] It was found that the relative strengths obtained were approximately the same with different indicators, and that the titration curves for a given acid were the same when the titration was carried out with different strong bases. This seems to indicate that the changes investigated actually do involve a proton transfer, though the low dielectric constant of the medium obscures many of the usual properties of the salts formed. It is a striking fact that the order of acid strengths found is essentially the same as in water. The results are, however, very difficult to interpret exactly, as the acid–base systems (including the indicators) are often associated to a great extent; thus all carboxylic acids exist essentially as double molecules in these solvents.[45] This probably accounts for some of the anomalous results; *e.g.*, LaMer and Downes found titration and dilution curves having half the theoretical slope. Owing to the absence of free ions, the electrostatic effects considered by Wynne-Jones will be at any rate much reduced, which may explain why the relative strengths are found to be roughly the same as in water, in spite of the very low dielectric constant. R. P. B.

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[40] Cf. also J. N. Brönsted, *Z. physikal. Chem.*, 1934, **169**, 52; *A.*, 962.

[41] *Ber.*, 1928, **61**, 2049; *A.*, 1928, 1188.

[42] *J. Amer. Chem. Soc.*, 1933, **55**, 1840; *A.*, 1933, 675.

[43] *Ber.*, 1929, **62**, [*B*], 970; *A.*, 1929, 666.

[44] V. K. LaMer and H. C. Downes, *J. Amer. Chem. Soc.*, 1931, **53**, 888; *A.*, 1931, 584.

9. Miscellaneous Subjects.

The range of subject matter studied during the past year and not included in the foregoing sections of this report is a wide one, and reference can only be made in broad outline to the more prominent lines of investigation.

The application of *X*-ray and electron-diffraction methods to the determination of molecular structures has been extended to a large variety of compounds.[1] Attention should also be drawn to two discussions held during the year; in one,[2] dipole-moment measurements have been considered in reference to molecular structure, and such matters as the resonance between linkages in molecules and free rotation have been examined; in the other,[3] free radicals of varying life have been described and discussed in different connexions. Reference should also be made to two accounts on subjects not easily accessible or frequently understood: D. C. Darrow has described briefly the essential principles of the wave and quantum mechanics,[4] and J. C. Slater has dealt with the electron theory of metals.[5] The theory of the Alternative Atom, suggested by J. Tutin,[6] has proved unserviceable.[7]

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[45] Cf. R. P. Bell, E. C. Baughan, and M. W. Vaughan-Jackson, *J.*, 1934, 1969.

[1] See, *e.g.*, S. B. Hendricks, L. R. Maxwell, V. R. Mosley, and M. E. Jefferson, *J. Chem. Physics*, 1933, **1**, 549; *A.*, 1934, 17; F. L. Arnot, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 360; *A.*, 577; F. B. Slagle and E. Ott, *J. Amer. Chem. Soc.*, 1933, **55**, 4396, 4404; *A.*, 1934, 17; R. W. Dornte, *J. Chem. Physics*, 1933, **1**, 566, 630; *A.*, 18; W. C. Pierce, *ibid.*, **2**, 1; *A.*, 244; O. Stelling, *Z. physikal. Chem.*, 1934, [*B*], **24**, 282; *A.*, 352; W. T. Astbury and H. J. Woods, *Phil. Trans.*, 1933, [*A*], **232**, 333; *A.*, 352; R. O. Jenkins, *Phil. Mag.*, 1934, [vii], **17**, 457; *A.*, 352; L. Pauling and J. Sherman, *Proc. Nat. Acad. Sci.*, 1934, **20**, 340; *A.*, 948; (Sir) W. H. Bragg, *Nature*, 1934, **134**, 138; *A.*, 948; J. M. Robertson. *Proc. Roy. Soc.*, 1934, [*A*], **146**, 473; *A.*, 1297; M. L. Huggins and J. E. Mayer, *J. Chem. Physics*, 1933, **1**, 643; *A.*, 1934, 16; see also (Sir) W. H. Bragg, *Proc. Roy. Inst.*, 1934, **28**, 57; *A.*, 478; *Trans. Faraday Soc.*, 1934, **30**, 665.

[2] *Ibid.*, pp. 679—900.

[3] *Ibid.*, pp. 3—245.

[4] *Rev. Mod. Physics*, 1934, **6**, 23.

In the following, an attempt has been made to classify various topics under appropriate headings.

Emission of Electrons in Chemical Change.—A. K. Denisoff and O. W. Richardson [8] have continued their interesting work on the emission of electrons under the influence of chemical reaction, a phenomenon not discussed for some time in these Reports. It has long been known that when the sodium–potassium alloy, NaK_2, is brought into contact with certain reactive gases such as halogens or carbonyl chloride, at low pressure, electrons are emitted. More detailed examination now shows that each of a variety of gases or vapours may be used, *e.g.*, carbonyl chloride, chlorine, bromine, iodine, nitrosyl chloride, carbonyl sulphide, sulphur chlorides, sulphuryl chloride, mercuric chloride. With gaseous hydrogen chloride or with steam, the effect is less marked, and with nitrous oxide apparently absent. It is found that the electron emission increases uniformly with pressure up to a certain value, falling off again at higher pressures. The distribution of energy among the emitted electrons is not Maxwellian, but of a similar form, having a maximum. The important result is that the emission yield decreases as the available energy produced from the chemical reaction decreases, so that $E_{\text{max.}} = E_{\text{chem.}} - \phi$, where $E_{\text{max.}}$ is the maximum energy of an electron, $E_{\text{chem.}}$ the chemical energy derivable from the reaction, and ϕ is the work function of the metal. Denisoff and Richardson consider that, in general, a polar bond is first formed, this being stabilised by a three-body collision with the free metallic electron, which subsequently takes away all the surplus reaction energy. The relationship given above at once recalls the photoelectric effect. Assuming its general validity, a determination of $E_{\text{max.}}$ for any given reaction may lead to a deduction of $E_{\text{chem.}}$, which in its turn may provide the criterion for deciding which of several possible elementary processes is involved in the reaction. It is therefore clear that these experiments have, in a limited way at least, some importance in connexion with the kinetics of heterogeneous chemical reactions.

Spectroscopic Considerations.—Perhaps the greatest accumulation of experimental data has occurred in that field which deals with the study of chemicophysical problems by the methods of spectroscopy. The infra-red and ultra-violet absorption spectra of many inorganic and organic polyatomic molecules have been measured, both in the vapour and the liquid state.[9] The primary objects of such work are to determine the stereochemical and electronic structures of the molecules, the energies of linkage, and the mechanism of chemical reactions which the molecules undergo; the principles involved have been discussed in previous Reports.[10] A comparison of the spectra of some simple molecules containing hydrogen H^1 with the corresponding compounds of deuterium H^2 has been made (this vol., p. 15).

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[5] *Rev. Mod. Physics*, 1934, **6**, 209.

[6] "The Atom," Longmans, 1934.

[7] R. H. Fowler, *Nature*, 1934, **133**, 852.

[8] *Proc. Roy. Soc.*, 1934, **144**, [*A*], 46; *A.*, 468; *ibid.*, **146**, [*A*], 524; *A.*, 1282; *ibid.*, **145**, [*A*], 18; *A.*, 937; cf. also F. Haber and K. Just, *Ann. Physik*, 1911, **36**, 308.

A catalogue of the new material would exceed the scope of this Report, but in any case discussion would be premature until it has become more systematised and the theoretical aspects more clearly understood. A particularly interesting study is that of the absorption spectrum of the volatile osmium tetroxide, OsO_4;[11] and a somewhat unusual method has been employed by G. B. Kistiakowsky and H. Gershinowitz[12] in the determination of the C–C linkage energy in cyanogen molecules. From measurements of the pressures at which absorption bands due to CN, produced by the dissociation of cyanogen at different temperatures in the region of 1200°, have equal intensity, these workers obtain a value of 77 ± 4 kg.-cals. per g.-mol., which agrees well with existing thermochemical data. From measurements on absolute intensity of the infra-red vibration bands of hydrogen halide gases, E. Bartholomé[13] concludes that these molecules contain a homopolar link. The limitations, indicated previously, of the use of spectral measurements in deciding the mechanism of photochemical primary processes have again been emphasised by several authors;[14] measurements on fluorescence taken in conjunction with the spectral data, although essential, may also prove not unambiguous.

More examples have been reported of the emission spectra of highly ionised atoms. Typical examples are those of Bi iv, O iii, F ii iii iv, Br v vi vii, Cl iii iv v, Sb ii iii, Au ii, Ra ii, S ii, C iii. H. Beutler and K. Guggenheimer [15] have studied the absorption spectra of the vapours of mercury, cadmium, zinc, potassium, and cæsium in the extreme ultra-violet; these arise from an excitation of inner electrons and frequently involve levels which "predissociate" into an electron and ionised atoms.

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[9] See, *e.g.*, H. Conrad-Billroth, *Z. physikal. Chem.*, 1933, **23**, [*B*], 315; *A.*, 1934, 8; R. Schaffert, *J. Chem. Physics*, 1933, **1**, 507; *A.*, 1934, 9; H. Vedder and R. Mecke, *Z. Physik*, 1933, **86**, 137; *A.*, 1934, 9; G. Hettner, R. Pohlman, and H. J. Schumacher, *Naturwiss.*, 1933, **21**, 884; *A.*, 1934, 129; P. K. Sen-Gupta, *Proc. Roy. Soc.*, 1934, [*A*], **143**, 438; *A.*, 237; J. Lecomte, *Compt. rend.*, 1934, **198**, 65; *A.*, 238; G. H. Dieke and G. B. Kistiakowsky, *Physical Rev.*, 1934, [ii], **45**, 4; A. Glissmann and H. J. Schumacher, *Z. physikal. Chem.*, 1934, **24**, [*B*], 328; *A.*, 344; H. W. Thompson and A. P. Garratt, *J.*, 1934, 524; *A.*, 582.

[10] *Ann. Reports*, 1933, **30**, 79; 1932, **29**, 47; 1931, **28**, 367; 1930, **27**, 21.

[11] A. Langseth and B. Quiller, *Z. physikal. Chem.*, 1934, **27**, [*B*], 79.

[12] *J. Chem. Physics*, 1933, **1**, 432; *A.*, 1934, 30.

[13] *Z. physikal. Chem.*, 1933, **23**, [*B*], 131; *A.*, 1933, 1227.

[14] Cf. Royal Society Discussion on Energy Distribution, *Proc. Roy. Soc.*, 1934, **146**, [*A*], 239.

The existence of the polarisation molecule O_4, originally suggested by G. N. Lewis [16] from measurements on the magnetic properties of liquid oxygen, has now been examined by spectral methods, consisting essentially in an analysis of the absorption spectrum of highly compressed oxygen gas or of the liquid. W. Steiner,[17] H. Salow and W. Steiner,[18] and R. Guillien,[19] have now established the existence of this complex. W. Finkelnburg [20] has summarised critically all the relevant data on the subject, and from an analysis of the absorption bands at high pressures has obtained a value for the O_2–O_2 link energy of some hundredths of a volt, *i.e.*, *ca.* 0·2 kg.-cal. per g.-mol., in fair agreement with Lewis's original value. It seems probable that other similar polarisation molecules exist, the failure to detect them being due to difficulties of obtaining the requisite conditions.

From an analysis of a new hydrogen resonance spectrum in the far ultra-violet, obtained in a discharge tube containing hydrogen and argon, H. Beutler [21] has determined the energies of dissociation of hydrogen H^1_2, deuterium H^2_2, and of H^1H^2. The values per g.-mol. are 102·7, 104·5, and 103·5 kg.-cals. From a consideration of certain predissociation phenomena in nitrogen bands reported by A. van der Ziel,[22] G. Herzberg and H. Sponer [23] have recalculated the energy of dissociation of the nitrogen molecule and obtain a value 169·3 kg.-cals. per g.-mol.

P. K. Sen-Gupta [24] has considered the different types of absorption spectrum from the standpoint of the Franck–Condon principle. The spectroscopic examination of the flame spectrum of ethylene [25] suggests the presence of an emitting molecule HCO.

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[15] *Z. Physik*, 1933, **86**, 495, 710; **87**, 19, 176, 188; 1934, **88**, 25; *A.*, 1934, 3, 124, 231, 467, 1280.

[16] *J. Amer. Chem. Soc.*, 1924, **46**, 2027.

[17] *Trans. Faraday Soc.*, 1934, **30**, 34; *A.*, 242.

[18] *Z. Physik*, 1934, **90**, 11; *A.*, 1055; *Nature*, 1934, **134**, 463; *A.*, 1153.

[19] *Compt. rend.*, 1934, **198**, 1223, 1486; *A.*, 472, 580.

[20] *Z. Physik*, 1934, **90**, 1; *A.*, 1055.

[21] *Z. physikal. Chem.*, 1934, **27**, [*B*], 287.

[22] *Nature*, 1934, **133**, 416.

[23] *Z. physikal. Chem.*, 1934, **26**, [*B*], 1.

[24] *Z. Physik*, 1934, **88**, 647; *A.*, 715.

[25] W. M. Vaidya, *Proc. Roy. Soc.*, 1934, **147**, [*A*], 513.

The Neutrino (see also p. 394).—In the construction of a theory of nuclear electrons and β-ray emission there are two difficulties, first the continuous nature of the β-ray spectrum, and secondly the fact that the theory of relativity of light particles cannot explain satisfactorily how electrons may remain bound in orbits with dimensions of nuclear magnitude. The latter difficulty would disappear if the nuclei contained no electrons, and this is the essential feature of Heisenberg's theory, which regards the nucleus as built up of protons and neutrons. If, however, the process of β-ray emission is to be regarded as a quantum process, it is difficult to reconcile the continuous β-ray spectrum with the law of conservation of energy. Fermi has accordingly suggested that simultaneously with the emission of a β-particle, another particle is emitted, of mass comparable with, or less than, that of the electron and carrying no charge. The process of β-ray decay is then

$$\text{neutron} \longrightarrow \text{proton} + \text{electron} + \text{neutrino.}$$

A comparison of this process with that involving the emission of radiation from an excited atom leads to a calculation of the decomposition probability, *i.e.*, the life of the neutron state. Fermi has also obtained a relationship, similar in nature to the Geiger–Nuttall equation for α-ray decay, which expresses the variation of the maximum momentum of β-particles emitted by a given element with its average life. Again, by analogy with "probable" or "forbidden" transitions in the theory of radiation, it is found here that the radioactive elements should, as regards β-ray decay, fall into two groups, the one of short life, the other of long life. Examination of the experimental data supports this conclusion. Details are given elsewhere in these Reports.

Nuclear Moments.—Measurements of the mechanical and magnetic moments of nuclei from hyperfine structure or the polarisation of resonance radiation have rapidly multiplied since the last Report.[26] Typical cases studied are Be, Xe, Na, Ta, P, Zn, Te, Se, Sb, Sn.[27]

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[26] *Ann. Reports*, 1934, **30**, 76.

[27] See, *e.g.*, E. Gwynne-Jones, *Nature*, 1933, **132**, 781; *A.*, 1934, 2; L. P. Granath and C. M. van Alta, *Physical Rev.*, 1933, [ii], **44**, 935; *A.*, 124; M. F. Ashley, *ibid.*, p. 919; *A.*, 124; D. A. Jackson, *Proc. Roy. Soc.*, 1934, **143**, [*A*], 455; A. B. McLay and M. F. Crawford, *Physical Rev.*, 1933, [ii], **44**, 986; H. Kopfermann and E. Rindall, *Z. Physik*, 1934, **87**, 460; *A.*, 339; F. Paschen and I. S. Campbell, *Naturwiss.*, 1934, **22**, 136; *A.*, 467; J. Joffe, *Physical Rev.*, 1934, [ii], **45**, 468; *A.*, 575; S. Tolansky, *Nature*, 1934, **133**, 531; *A.*, 576; *Proc. Roy. Soc.*, 1934, **146**, [*A*], 182; *A.*, 1147; D. A. Jackson and H. Kuhn, *Nature*, 1934, **134**, 25; *A.*, 823; E. G. Jones, *Proc. Roy. Soc.*, 1934, **144**, [*A*], 587; *A.*, 823; O. E. Anderson, *Physical Rev.*, 1934, [ii], **45**, 685; *A.*, 824; *ibid.*, **46**, 473; *A.*, 1280.

In view of the unsatisfactory state of the theory of nuclear structure, it is not surprising that the new values often found are not easily explained. General discussions of the subject have been given by E. Fermi and E. Segrè,[28] by W. E. Curtis,[29] by H. Kallmann and H. Schüler,[30] by G. Gamow,[31] and others (see also this vol., p. 372).

The most significant measurements in this field relate to those structures which might prove to be elementary particles in the process of atom-building, *viz.*, the proton, deuton, and neutron; the electron-spin moment has long been taken as $\frac{1}{2}$ Bohr unit in order to fit spectral requirements. Details of these measurements are fully reported elsewhere (p. 372).

Consideration of the law of conservation of angular momentum in nuclear disintegration processes may also be used to determine nuclear-spin moments. In this manner H. Raether [32] estimates the neutron mechanical moment to be $\frac{1}{2}$ Bohr nuclear unit. D. R. Inglis and A. Landé,[33] assuming values of magnetic moments of higher nuclei, in this way find that the magnetic moment of the proton should be 2, the spin moment of the neutron $\frac{1}{2}$, and the magnetic moment of the neutron $-0{\cdot}6$ unit. I. Tamm and S. Altschuler's [34] value agrees with the latter, but H. Schüler [35] obtains a different result.

The Structure of Liquids.—The phenomenon of crystalline liquids or "liquid crystals" has long been known. The belief that "amorphous," optically isotropic liquids also possess some spatial orderly arrangement has become prevalent only during the past few years,[36] largely from measurements on the diffraction of *X*-rays by these liquids. This orderly structure has been called a "cybotactic" condition; references to earlier work on the subject are given in C. Drucker's summarising article.[37]

A variety of molecule types have now been studied, *e.g.*, chain molecules such as *n*-alcohols, *n*-fatty acids, *n*-paraffins, benzene and *cyclo*hexane derivatives. The results lead to deductions of the diameter of carbon chains, distance between adjacent carbon atoms, thickness of benzene rings, and of the occurrence of associated molecules in solution. As an instrument for investigating the nature of different types of electrolytic solution, the method promises to be of some importance.

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[28] *Mem. R. Accad. d'Italia Sci. fis.*, 1933, **4**, 131; *A.*, 231.

[29] *Nature*, 1934, **133**, 256; *A.*, 340.

[30] *Z. Physik*, 1934, **88**, 210, 323; *A.*, 580.

[31] *Ibid.*, **89**, 592; *A.*, 939; *Nature*, 1934, **133**, 833; *A.*, 715; *Proc. Roy. Soc.*, 1934, **146**, [*A*], 217; *A.*, 1152; see also K. Guggenheimer, *J. Phys. Radium*, 1934, **5**, 475; *A.*, 1284.

[32] *Naturwiss.*, 1934, **22**, 151.

[33] *Physical Rev.*, 1934, **45**, 842.

[34] *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **1**, 455; *A.*, 580.

[35] *Z. Physik*, 1934, **88**, 323.

[36] G. W. Stewart, *Chem. Reviews*, 1929, **6**, 483; *Rev. Mod. Physics*, 1930, **2**, 116; other references are given by H. K. Ward, *J. Chem. Physics*, 1934, **2**, 153.

[37] *Physikal. Z.*, 1928, **29**, 373.

G. W. Stewart[38] has studied the case of concentrated solutions of lithium chloride in ethyl, propyl, and butyl alcohols. It appears that in these solutions both lithium and chlorine ions participate with the molecules of the solvent in forming a common liquid cybotactic structure, and also that the solutions are really solutions of the alcoholates of the lithium chloride above the corresponding transition temperatures. The temporary cybotactic structures can be regarded as similar to ionic crystals, conduction in which has definite similarities to conduction in electrolytes.

Stewart[39] has also applied the method to the analysis of water and of deuterium oxide. The results are discussed in connexion with the ideas of J. D. Bernal and R. H. Fowler[40] on the liquid structure of water. N. S. Guigrich and B. G. Warren[41] have shown theoretically that existing calculations for the intensity of *X*-rays diffracted by a fluid at various densities should only be applied over a small range of density. Comparison is made with the experimental results of Stewart[42] with ether. W. Kast[43] has compared the *X*-ray diagrams given by the isotropic and anisotropic melt of *p*-azoxyanisole. There is no appreciable difference, from which it is concluded that in both cases groups of oriented molecules exist with approximately the same molecular aggregation. R. D. Spangler[44] has attempted to follow with ether the change from a cybotactic state to the random arrangement of a gas as conditions of pressure and temperature are altered.

Optical Activity.—According to the original theory of Pasteur, optical activity of a molecule appears when the structure is so unsymmetrical that it cannot be superposed upon its mirror image; one enantiomorph is dextro-, the other lævo-rotatory. The question of the "absolute" configuration, *i.e.*, which of the two mirror images is dextro- and which lævo-rotatory, is not discussed. So long as no hypotheses regarding the origin of optical rotatory power were available, the question was not answerable. With the introduction of some theory which can explain the reasons for the power of optical rotation, it might be possible to assign the individual "absolute" configurations of the enantiomorphs.

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[38] *J. Chem. Physics*, 1934, **2**, 147; *A.*, 591.

[39] *Ibid.*, p. 558.

[40] *Ibid.*, 1933, **1**, 515; *A.*, 1934, 13; *Ann. Reports*, 1933, **30**, 34.

[41] *Physical Rev.*, 1934, **46**, 248.

[42] *Trans. Faraday Soc.*, 1933, **29**, 982.

[43] *Naturwiss.*, 1933, **21**, 737; *Ann. Physik*, 1934, [v], **19**, 571; *A.*, 478.

[44] *Physical Rev.*, 1934, [ii], **46**, 698; *A.*, 1297.

W. Kuhn and K. Bein[45] have made a valuable contribution to this subject. By means of models, the optically active behaviour of compounds of the type of pentaerythritoldipyruvic acid, potassium cobalt oxalate, $K_3[Co(C_2O_4)_3]$, and the compound $[Co\,en_3]Br_3$, (en = ethylenediamine), in absorption bands in the near ultra-violet and visible region has been calculated. The fundamental assumption is that the coupling forces which are effective between the various parts of the molecule in optical oscillations can be deduced, at least as far as sign is concerned, from the polarisability of the various parts of the molecule and the vibrational scattering moments in the adjoining parts. This affords a semi-quantitative explanation of the observed behaviour of the potassium cobalt oxalate complex. Relations are deduced permitting the calculation of the anisotropy factor of an absorption band having a scattering moment of any form. With asymmetric compounds the optical activity of which is due to unsymmetrical arrangement of like symmetrical parts, the absorption bands are resolved into parts the anisotropy factors of which for a given band differ in magnitude and at times in sign. This has been detected with the two absorption regions of the double oxalate in the visible region, and from a comparison of the optical properties of this compound with those of a model, it has been possible to deduce the absolute configuration of the isomeride which is lævorotatory in sodium D light (and dextrorotatory in red light). The conclusions are confirmed by measurements of the absorption, rotation, and circular dichroism in the range 2600—9000 Å.

Valency and the Structure of Molecules.—In continuation of matters reported upon last year, several papers have dealt with the electronic structure of molecules by the methods of quantum mechanics. M. Markov[46] has considered the benzene molecule as composed of six tervalent nitrogen-like CH groups, and by applying the Heitler–London–Rumer theory of valency, has investigated the mechanical and thermodynamical stability of the structure. W. G. Penney[47] has examined the energy of $(CH)_n$ structures in general, and concludes that C_6H_6 is the most stable, is slightly buckled, and should be easily hydrogenated. In discussing the structure of hydrogen peroxide and of hydrazine, W. G. Penney and G. B. B. M. Sutherland[48] have concluded that the large dielectric moments of these compounds are due to an unsymmetrical form and not to free rotation. W. G. Penney [49] has shown that in ethylene all six nuclei should be coplanar, and in ethane only the H–H repulsion prevents free rotation of the methyl groups about the C–C axis. J. H. van Vleck [50] has discussed the electronic states of the carbon atom with special reference to the structure of methane. According to this author, the ^5S state of carbon probably lies 7 volts above the ground state. The method of the Hartree self-consistent field has been applied to K^+, Cs^+, and C.[51] The molecule Li_2 has been studied wave-mechanically.[52] R. S. Mulliken [53] has attempted to construct an " absolute " scale of electronegativity for the elements by taking the average of ionisation potential and electron affinity. The electro-affinity of an atom has different values for different values of its valency, in general being higher for higher valencies. The scale calculated for many elements agrees well with that of Pauling based on thermal data. L. Pauling and G. W. Wheland, and L. Pauling and J. Sherman, have applied the idea of resonance between links in molecules to the determination of the structure of benzene and naphthalene. These matters are discussed on p. 37. N. V. Sidgwick and R. W. Bailey [53a] have drawn some interesting correlations between the structures of carbonyls and nitrosyls. The three-electron bond has been discussed in connexion with potassium superoxide.[54]

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[45] *Z. physikal. Chem.*, 1934, **54**, [*B*], 335; *A.*, 476; *Ber.*, 1933, **66**, 166; see also S. F. Boys, *Proc. Roy. Soc.*, 1934, **144**, [*A*], 655, 675; *A.*, 832.

[46] *J. Chem. Physics*, 1933, **1**, 784; *A.*, 1934, 133.

[47] *Proc. Roy. Soc.*, 1934, **146**, [*A*], 223; *A.*, 1158.

[48] *Trans. Faraday Soc.*, 1934, **30**, 898; *A.*, 1158; *J. Chem. Physics*, 1934, **2**, 492; *A.*, 1158.

Several papers relate to the theory of " normal " vibrations of polyatomic molecules.[55] In connexion with the empirical analysis of the energy levels of isoelectronic diatomic molecules, the study of the 22-electron molecule PN is of interest.[56] The data for this molecule are similar to those of the isoelectronic SiO and CS, and are intermediate between the 14-electronic N_2 and CO and 30-electronic P_2 molecules in all important features.

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[49] *Proc. Roy. Soc.*, 1934, **144**, [*A*], 166; *A.*, 476.

[50] *J. Chem. Physics*, 1933, **1**, 177, 219; *A.*, 13; *ibid.*, 1934, **2**, 20, 297; *A.*, 241, 719.

[51] D. R. Hartree, *Proc. Roy. Soc.*, 1934, **143**, [*A*], 506; *A.*, 344; *Physical Rev.*, 1934, [ii], **46**, 738; *A.*, 1285; C. C. Torrance, *ibid.*, p. 388; *A.*, 1153; cf. *Ann. Reports*, 1933, **30**, 62.

[52] E. B. Wilson, *J. Chem. Physics*, 1933, **1**, 210; *A.*, 1934, 1; H. M. James, *ibid.*, 1934, **2**, 794.

[53] *Ibid.*, p. 782.

[53a] *Proc. Roy. Soc.*, 1934, [*A*], **144**, 521; *A.*, 833.

[54] E. W. Neuman, *J. Chem. Physics*, 1934, **2**, 31; *A.*, 242.

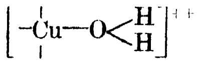
[55] See, *e.g.*, E. B. Wilson, *Physical Rev.*, 1934, [ii], **45**, 706; *A.*, 829; A. Eucken and H. Ahrens, *Z. physikal. Chem.*, 1934, [*B*], **26**, 297; *A.*, 1055.

[56] J. Curry, L. Herzberg, and G. Herzberg, *Ann. Physik*, 1934, [v], **20**, 569; *A.*, 1153; *J. Chem. Physics*, 1933, **1**, 749; *A.*, 1934, 7; *Z. Physik*, 1933, **86**, 348; *A.*, 1934, 7; see also W. Jevons, *Nature*, 1934, **133**, 619; *A.*, 581.

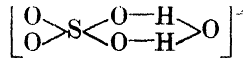
The electronic theory of valency has been criticised and theories of valency in general discussed by R. Samuel and others.[56a] These authors believe that valency is always covalency and may vary in polarisability from zero to that of a true salt. They do not admit the existence of co-ordinate links in such molecules as carbon dioxide or the complex cyanides. They point out that the inner (S^2) group of electrons usually considered responsible for co-ordinate valency formation cannot enter into chemical union with other atoms until split, *i.e.*, until the atom containing this group is excited, and they define valency as the passage of electrons from each participating atom into a closed group in the molecule. From a review of spectroscopic and thermochemical data R. Samuel and H. Lessheim [56b] conclude that many molecules are produced by union of atoms in anomalous states of excitation. In the case of carbon dioxide the necessary state of the carbon atom is thought to be p^4, *i.e.*, not s^2p^2 or sp^3. Carbon monoxide, arising from the s^2p^2 configuration, in which only two p electrons will be used, is regarded as involving a bivalent link. It is impossible to enter into further details of this subject. Many differences of opinion expressed are ultimately attributable to differences in definition and certain of the linkage energies deduced may be inaccurate. R. S. Mulliken [56c] also has discussed the structure of carbon monoxide.

An ingenious experiment has been made by J. N. E. Day, E. D. Hughes, C. K. Ingold, and C. L. Wilson [57] in which the difference in properties of water and heavy water was used in investigating the structure of salt hydrates. It has been commonly supposed that cationic hydration occurs by means of a metal–oxygen co-ordinate link (I), whereas anionic hydration involves co-ordination with the hydrogens of the water molecule (II).

(I.)



$$\left[-\mathrm{Cu}-\mathrm{O}{<}^{\mathrm{H}}_{\mathrm{H}}\right]^{++}$$



$$\left[{}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{S}{<}^{\mathrm{O-H}}_{\mathrm{O-H}}{>}\mathrm{O}\right]^{-}$$

(II.)

The alternative theory of Fajans, Born, and others regards the hydrate more as a physical cohesion of dipoles. If the co-ordination theory applies, the nature of the hydrogen atoms in the water molecule should not much affect cationic hydration, but with anionic hydrate there will be a preferential hydration between light and heavy water. The experiments aim at detecting this effect, but the results cannot be regarded as conclusive. If any inferences can be drawn from them, it would be that the physical theory of hydration is supported, the linkings of the hydrate having a very loose nature.

[56a] R. F. Hunter and R. Samuel, *J.*, 1934, 1180; *A.*, 1058; H. Lessheim and R. Samuel, *Z. Physik*, 1933, **84**, 637; *Current Sci.*, 1933, 374; R. Samuel and M. J. Kahn, *Z. Physik*, 1933, **84**, 87.

[56b] *Proc. Physical Soc.*, 1934, **46**, 523; *A.*, 945.

[56c] *J. Chem. Physics*, 1934, **2**, 400; *A.*, 942.

[57] *J.*, 1934, 1593; *A.*, 1303.

Supersonic Waves.—The rapid degradation of intensity suffered by compressional waves of high frequency when passing through gases, was first observed by W. C. Pierce [58] in carbon dioxide. The determination of the velocity of such supersonic waves, produced from piezoelectric quartz oscillators, and their dispersion by gases in general, has received considerable attention in recent years.[59]

This dispersion may be ascribed to one or more of three causes: (*a*) there may be a lag in the transfer of energy between one and another of the degrees of freedom of the molecule, (*b*) selective or resonant absorption may occur, (*c*) there may be an abnormal viscosity under the high-frequency vibration.

It is perhaps by virtue of the factor (*a*) that this subject is of interest and importance to those concerned with chemical kinetics.[60] The theory of the propagation of sound waves in a gas, with special reference to the intramolecular energy transfers, has been examined recently by several workers.[61] Long ago, (Sir) J. H. Jeans [62] showed that in a gas in which there was a delay in the passage of translational energy into vibrational energy, the velocity of sound would be higher than normal, owing to the enhanced ratio of the specific heats, if the source of sound had a period comparable with the "time of relaxation." This would involve a diminishing amplitude of the waves. When the period of oscillation approaches the relaxation time, there should be a rapid rise in the velocity of propagation.

E. G. Richardson [63] has examined the dispersion of supersonic waves in oxygen, carbon dioxide, nitrous oxide, sulphur dioxide, and argon. His results as a whole substantiate the Jeans relaxation-time theory, *i.e.*, cause (*a*), but there may be some indications of selective resonant absorption at frequencies considerably lower than those hitherto considered possible. It is interesting to observe that in some cases there was a marked scattering of the radiant energy, an effect, moreover, which was most pronounced with strongly anisotropic molecules which show the Raman effect most readily.

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[58] *Proc. Amer. Acad. Sci.*, 1928, **43**, 375.

[59] For a general account, see J. Hubbard, *J. Acoust. Soc.*, 1932, **4**, 99; also W. H. Pielemeier, *Physical Rev.*, 1929, **34**, 1184; 1930, **36**, 1005; 1931, **38**, 1236; 1932, **41**, 833; T. P. Abello, *Physical Rev.*, 1928, **31**, 1083; *A.*, 1928, 828; H. Kneser, *Ann. Physik*, 1931, **11**, 761, 777; *Z. Physik*, 1932, **77**, 649; E. Grossmann, *Ann. Physik*, 1932, **13**, 681.

[60] Cf. *Ann. Reports*, 1933, **30**, 39.

[61] K. F. Herzfeld and O. K. Rice, *Physical Rev.*, 1928, **31**, 691; A. Bourgin, *Phil. Mag.*, 1929, **7**, 821; H. Kneser, *Ann. Physik*, 1931, **11**, 761; W. T. Richards, *J. Chem. Physics*, 1933, **1**, 863, 879; *A.*, 1934, 135.

[62] "Dynamical Theory of Gases," p. 320 (1904).

[63] *Proc. Roy. Soc.*, 1934, **146**, [*A*], 56; *A.*, 1164.

H. H. Rogers [64] has made similar measurements on the absorption of supersonic waves in mixtures of air and carbon dioxide containing different amounts of water vapour.

W. T. Richards and J. A. Reid,[65] in very detailed papers, have gone further by attempting to discover how the translational energy of the sound wave is selectively transformed into vibrational energy of different types (symmetric or deformation vibrations, S←C→S, S↓C↑S↓) in the molecules carbon dioxide, carbon disulphide, and sulphur dioxide. They have also measured the velocity of sound in ethylene at various pressures, temperatures, and frequencies, and conclude that with this substance equilibrium is attained between the various states of vibrational energy in every effective collision, but that considerable activation energy of collision is required for the conversion of translational into vibrational energy. Collisions with argon, helium, or nitrogen molecules have no appreciable effect on the vibrational energy of the ethylene molecule. Collisions with hydrogen are about ten times as effective as ethylene–ethylene collisions in producing transitions in the lower vibrational energy states of ethylene. It is peculiar that ethylene–hydrogen mixtures appear to be about twenty times as effective as hydrogen–hydrogen collisions in exciting the rotational energy of hydrogen molecules.

J. Franck and A. Eucken [66] also have studied the conversion of translational kinetic energy into internal energy of vibration, and attempt to consider the problem from the standpoint of the " exchange " forces operative between the colliding partners rather than by classical methods involving laws of impact. From measurements on the dispersion of supersonic waves by chlorine and carbon dioxide, A. Eucken and R. Becker [67] have found that the transfer of energy of translation to intramolecular vibrations is in these cases favoured by the addition of inert gases.

Some similar experiments have been made with liquids.[68]

Optical Phenomena and Energy Transfers.—In addition to the foregoing, a series of optical considerations promises to clarify the mechanism of inter- and intra-molecular transfers of energy. The quenching of fluorescence by added inert gases has already been much studied, and further data are now reported.[69] In many cases specific properties seem to be involved, and the whole subject is far from clearly understood.

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[64] *Physical Rev.*, 1934, [ii], **45**, 208; *A.*, 354.

[65] *J. Chem. Physics*, 1933, **1**, 737; *A.*, 19; 1934, **2**, 193, 206; *A.*, 588.

[66] *Z. physikal. Chem.*, 1933, [*B*], **20**, 460; *A.*, 1933, 554.

[67] *Ibid.*, p. 467; *ibid.*, 1934, [*B*], **27**, 219, 235.

[68] J. C. Swansen, *J. Chem. Physics*, 1934, **2**, 689.

The quenching of inert gases of a different type of emission spectrum, however, appears to offer important data. It is possible from an analysis of the distribution of intensity in the rotational lines of a band in a molecular spectrum to determine the temperature of the emitting molecule.[70] Measurements of this kind on spectra emitted from discharge tubes have frequently revealed temperatures of some thousands of degrees, far higher than seems plausible.[71] O. Oldenberg[72] has discussed the interpretation of this result. When a polyatomic molecule is broken into fragments by some process such as takes place in a discharge tube, it is not difficult to understand how the fragments may fly apart each in a rapid state of rotation. Thus, if in the disrupture of the triangular water molecule one O–H bond is broken under extension, the hydroxyl radical liberated will possess surplus energy of rotation. The intensity distribution in the bands of hydroxyl formed in a discharge tube containing water vapour do, in fact, show " abnormal rotation." Oldenberg has found, however, that the addition of small quantities of helium removes the excess rotational energy so as to produce a normal temperature distribution; this gas is, moreover, specifically fitted for the purpose.

In the same way, the bands of HgH formed in the sensitised fluorescence of hydrogen by mercury have indicated a temperature of 3000° C.[73] H. Beutler and E. Rabinowitsch[74] concluded that this was due to " abnormal rotation "; the peculiarity is that nitrogen does not reduce the apparent temperature, and the surplus energy must be retained over many collisions.

O. S. Duffendack, R. W. Revans, and A. S. Roy[75] have also shown that added helium alters the distribution of intensities in the rotation lines in the bands of the N_2^+ spectrum. The question arises as to whether " abnormal vibration " is similarly possible. The examples given may, however, serve to indicate the nature of the work.

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[69] See, *e.g.*, J. F. Koehler, *Physical Rev.*, 1933, [ii], **4**, 761; *A.*, 2; N. A. Prileshaeva, *Compt. rend. Acad. Sci. U.R.S.S.*, 1933, 282; *A.*, 1934, 340; O. S. Duffendack and J. S. Owens, *Physical Rev.*, 1934, [ii], **46**, 417; *A.*, 1148; M. G. Evans, *J. Chem. Physics*, 1934, **2**, 445; K. Weber and M. L. Savić, *Z. physikal. Chem.*, 1934, [*B*], **24**, 68.

[70] L. S. Ornstein and W. R. van Wijk, *Z. Physik*, 1928, **49**, 315; *A.*, 1928, 930; W. Lochte-Holtgreven, *ibid.*, 1930, **64**, 443; 1931, **67**, 590.

[71] *Idem, ibid.*; O. Oldenberg, *Physical Rev.*, 1931, **37**, 1550; N. Thompson, *Proc. Physical Soc.*, 1934, **46**, 436; *A.*, 711.

[72] *Physical Rev.*, 1934, [ii], **46**, 210; *A.*, 1153.

[73] R. W. Wood and E. Gaviola, *Phil. Mag.*, 1928, **6**, 1191.

[74] *Z. physikal. Chem.*, 1930, [*B*], **8**, 403.

[75] *Physical Rev.*, 1934, [ii], **45**, 807; *A.*, 823.

The effect of inert gases on the absorption spectra of polyatomic molecules has also been studied.[76] This may prove to be a fruitful field of investigation. H. W. T.

R. P. Bell.
E. J. Bowen.
N. V. Sidgwick.
H. W. Thompson.
L. A. Woodward.

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[76] H. I. Agarbiceanu, *Compt. rend.*, 1933, **197**, 1198; *A.*, 1934, 2; P. C. Cross and F. Daniels, *J. Chem. Physics*, 1934, **2**, 6; *A.*, 238.

INORGANIC CHEMISTRY.

1. ATOMIC WEIGHTS.

THE separation from each other, by chemical means, of the scarcer members of the rare-earth group of elements is attended by so many difficulties that the finality of the values assigned to their atomic weights may well be questioned. For these elements, especially, the advantages of a control by physical methods are obvious, but since the examination in 1925,[1] of lanthanum, praseodymium, cerium, and neodymium in the first mass spectrograph, no data have been available until this year. F. W. Aston [2] has now succeeded in so improving the original method of accelerated anode rays, that he has been able to obtain with this series of elements the requisite intensity in the high-resolution mass spectrograph, and to determine the isotopic constitution and atomic weights of the remaining ten elements.

Considering the whole group of fourteen elements of atomic numbers 57 to 60 and 62 to 71, the elements of odd atomic numbers, *viz.*, La (57), Pr (59), Eu (63), Tb (65), Ho (67), Tm (69), Lu (71), all prove to be simple with the exception of europium, which consists of a nearly equal mixture of the isotopes 151 and 153. Of the even elements, samarium (62) was found to be the most complex, and to consist of seven isotopes. Neodymium, gadolinium, and ytterbium contain six isotopes each, and erbium and dysprosium four each.

The mass-spectrum values for the atomic weights agree closely with the international values for La, Ce, Pr, Eu, Dy, Yb, and Lu, but are smaller than the chemical values in the other seven cases. These discrepancies are discussed in another part of this volume.[3] Since terbium and thulium are simple elements and the twin lines of europium are well defined and easy to measure, the chemical values are almost certainly in error.

In the same paper, Aston calls attention to the case of osmium, for which he obtained the value of 190·31 [5] in 1931, which was distinctly lower than the then-accepted chemical value 190·9, but very considerably lower than the new value of 191·5 adopted by the International Committee in their last report.[4] It will be interesting to see whether further work on the chemical side confirms the higher figure, but up to the present, with the exception of tellurium, revision of the chemical atomic weights has invariably supported the results obtained with the mass spectrograph.

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[1] F. W. Aston, *Phil. Mag.*, 1925, **49**, 1191.

[2] *Proc. Roy. Soc.*, 1934, [*A*], **146**, 46; *A.*, 1150.

[3] P. 370.

[4] *J.*, 1934, 499.

[5] F. W. Aston, *Proc. Roy. Soc.*, 1931, [*A*], **132**, 487.

The redetermination of the atomic weights of niobium and tantalum by O. Hönigschmid [6] is another example of this, and has cleared up the discrepancy noticed in last year's report.[7] Tantalum bromide and niobium chloride were prepared in a high state of purity and, after vacuum sublimation, were weighed. They were then brought into solution, and the silver equivalent determined by standard procedure. The values obtained were Ta = 180·89, Nb = 92·91, in close agreement with Ta = 180·89, Nb = 92·90 found by Aston,[8] but very appreciably lower than the International values, 181·84 and 93·3 respectively. A detailed account of this work on niobium has been published by O. Hönigschmid and K. Wintersberger.[9] Other investigations published recently which confirm Aston's values are those on the atomic weight of molybdenum by the analysis and synthesis of its trioxide by R. Lautié,[10] which gave the value Mo = 96·01; and on the densities and atomic weights of krypton [11] and xenon by W. Heuse and J. Otto.[12] The latter work supports the value obtained previously for these two gases by H. E. Watson,[13] and by R. Whytlaw-Gray, H. S. Patterson, and W. Cawood [14] by microbalance methods.

Turning now to work along classical lines, there is not much to report since last year, but mention should be made of an important investigation by C. R. Johnson [15] on the atomic mass of sodium, in which a very careful and critical study was made of the errors inherent in the measurement of the ratios NaCl : Ag and NaCl : AgCl by standard methods. Special attention was paid in this research to accurate nephelometry and to the determination of the correct end-point both in titration and in the estimations of the washings. A potentiometric method was used in some cases to control the results of the nephelometer. Among the many points of detail studied may be mentioned the neutrality of the fused sodium chloride, adsorption and solubility of silver chloride, the presence of films of silver chloride or silver on the vessels used, and of invisible cracks in the Pyrex flasks and beakers which might have retained

[6] *Naturwiss.*, 1934, **22**, 463; *A.*, 937.

[7] *Ann. Reports*, 1933, **30**, 1.

[8] *J.*, 1932, 2888; *Nature*, 1932, **130**, 130.

[9] *Z. anorg. Chem.*, 1934, **219**, 161.

[10] *Compt. rend.*, 1933, **197**, 1730; *A.*, 127.

[11] *Physikal. Z.*, 1934, **35**, 57; *A.*, 234.

[12] *Ibid.*, p. 628; *A.*, 1053.

[13] *Nature*, 1931, **127**, 631; *A.*, 666.

[14] *Proc. Roy. Soc.*, 1931, [*A*], **134**, 7; *A.*, 1932, 106.

[15] *J. Physical Chem.*, 1933, **37**, 923; *A.*, 1934, 4; see also *A.*, 1933, 773.

traces of liquids. The result of six closely concordant experiments gave NaCl : Ag = 0·541817, and that of five gave the gravimetric ratio NaCl : AgCl = 0·40779. From each of these, by taking Ag = 107·880 and Cl = 35·457, the same value Na = 22·994 was obtained : a value slightly lower than the international figure, Na = 22·997.

G. P. Baxter and A. H. Hale[16] have determined the ratio $I_2O_5 : Na_2CO_3$. This is the first time since the work of T. W. Richards and C. R. Hoover,[17] who measured the ratio Na_2CO_3 : NaBr : Ag, that the atomic weight of carbon has been linked up with the silver standard. Richards and Hoover's ratios were unfavourable for the calculation of an accurate value for carbon, giving values ranging from 11·997 to 12·008. Baxter and Hales found, as the mean of nine closely concordant experiments, $I_2O_5 : Na_2CO_3$ = 3·14950, but unless the atomic weights of iodine and sodium are known to a very high degree of accuracy, that of carbon remains uncertain. If, for instance, we use the international values Na = 22·997 and I = 126·92, carbon becomes 12·005, but with Na = 22·994 and the same value for iodine, C = 12·010. The latest value for iodine is 126·917, determined by Hönigschmid and H. Striebel,[18] which agrees closely with the mass-spectrograph value of 126·91, but really, at the present time, the accuracy of experiment is insufficient to discriminate between these small differences.

Evidence of a more direct character supports the new and high value for carbon advanced by M. Woodhead and R. Whytlaw-Gray[19] in 1933. It will be remembered that these workers obtained C = 12·011 by a comparison of the limiting densities of carbon monoxide and oxygen with a microbalance, a value perceptibly greater than C = 12·007 found for the same ratio by E. Moles and M. T. Salazar[20] using the standard methods of comparing gas densities. The last two workers[21] have now published a new series of measurements of the densities of these two gases by an improved method, which gives as the atomic weight of carbon 12·0065. In the meantime, F. W. Aston[22] has compared photometrically the second-order lines at positions 6 and 6·5 of C^{12} and C^{13} and has found the isotopic ratio to be $C^{12} : C^{13}$ = 140 : 1, whence, allowance being made for the packing fraction and change of scale, the atomic weight of carbon = 12·0080. It may be mentioned that

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[16] *J. Amer. Chem. Soc.*, 1934, **56**, 615; *A.*, 469.

[17] *Ibid.*, 1915, **37**, 95; *A.*, 1915, ii, 96.

[18] *Z. anorg. Chem.*, 1932, **208**, 53; *Z. physikal. Chem.*, Bodenstein Festband, 1931, 282; *A.*, 1931, 1208.

[19] *J.*, 1933, 846; *A.*, 1933, 894.

[20] *Anal. Fís. Quím.*, 1929, **27**, 267; *A.*, 1931, 407.

[21] *Ibid.*, 1934 **32**, 954.

[22] *Nature*, 1934, **134**, 178; *A.*, 937.

F. A. Jenkins and L. S. Ornstein[23] found by a study of the bands of the Swan spectrum the ratio $C^{12} : C^{13} = 106 : 1$, which has been confirmed by the work of J. P. Tate, P. T. Smith, and A. L. Vaughan,[24] who found C^{13} present to the extent of 1%, which supports the higher value C = 12·011 although it is difficult to assess the probable error in these figures. There now seems, however, to be no reasonable doubt that the true chemical atomic weight of carbon lies close to 12·01 and that the international value of 12·00 is too low. Just recently, important new evidence has appeared which supports the high value. H. S. Patterson and W. Cawood,[25] using an improved microbalance technique, have compared the limiting densities of carbon dioxide, ethylene, nitrous oxide, carbon tetrafluoride, and oxygen and repeated part of their earlier work on methyl fluoride. The final results are: N = 14·007, C = 12·012 (from ethylene), C = 12·010 (from CO_2), F = 18·995 (from CF_4), and F = 18·995 (from CH_3F).

As a check on the method, the compressibilities of the gases were measured by means of an Andrews apparatus, as well as by the microbalance, and a good agreement obtained. The two values for fluorine agree very closely with F. W. Aston's value[26] of 18·996, and negative definitely the possibility of the existence of a higher isotope. The value for nitrogen is rather lower than 14·008, the accepted figure, and also than the recently published values of E. Moles and J. Sancho[27] from ammonia, N = 14·008, and of Moles and Salazar[21] from nitrogen itself, N = 14·0083. A full account of the work of Patterson and Cawood will appear shortly, but it may be stated that it has been carried out with every modern refinement and attention to detail.

The discovery that hydrogen is a mixed element and that the isotopes are easily separable has cast doubt on the accuracy of one of the fundamental atomic-weight ratios, *viz.*, that of O : H. The numerous determinations made of the atomic weight of hydrogen were summarised by E. Moles[28] in 1925, and the final mean calculated from the results of five different workers was found to be 1·00777. In all cases, the hydrogen was prepared by electrolysis of either acid or alkaline solutions, and usually was weighed on palladium. It is probable then that this hydrogen was deficient in the heavier isotope and that the mean atomic weight is too low. It seems unlikely that hydrogen of normal isotopic content was ever used in measuring this ratio, though the oxygen employed probably contained its isotopes in the usual proportions.

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[23] *Proc. K. Akad. Wetensch. Amsterdam*, 1932, **35**, 1212; *A.*, 1933, 333.

[24] *Physical Rev.*, 1933, [ii], **43**, 1054.

[25] *Nature*, 1935, in the press.

[26] "Mass Spectra and Isotopes," p. 150; *Proc. Roy. Soc.*, 1927, [*A*], **115**, 487.

[27] *Anal. Fis. Quim.*, 1934, **32**, 931.

[28] *Z. physikal. Chem.*, 1925, **115**, 61.

Now the ratio of the masses of O^{16} and H^1 has been determined with great exactness with the mass spectrograph by F. W. Aston[29] and by E. K. Bainbridge[30] and found to be 16·0000 : 1·00778. The mean mass number of chemical oxygen on the physical scale can be calculated if the proportion of the heavier isotopes is known. This has been determined spectroscopically by a number of different observers, who obtain values varying from $O^{18} : O^{16} = 1 : 1250$[31] to 1 : 630,[32] the proportion of O^{17} being negligible. Of these, the second ratio is generally regarded as the most probable, and gives a value of 16·0035 for the atomic weight of chemical oxygen on the physical scale. Hence pure H^1 or protium has an atomic weight on the chemical scale of $1{\cdot}00778 \times 16{\cdot}0000/16{\cdot}0035 = 1{\cdot}00756$. If, now, we know the proportions of the two hydrogen isotopes present normally in the element, we can calculate the atomic weight. Unfortunately, the data on this point are not very concordant. The earlier spectroscopic estimates of W. Bleakney,[33] of H. Kallmann and W. Lasareff,[34] and of J. T. Tate and P. T. Smith[35] were too low and gave values for D : H of 1 : 30,000 to 1 : 40,000. G. N. Lewis[36] and R. T. Macdonald,[37] from their experiments on the electrolytic preparation of heavy water, calculate 1 : 6500. W. Bleakney and A. J. Gould[38] have recently redetermined the ratio spectroscopically, using hydrogen from rain water, which was decomposed completely by passage over heated iron; they found the value 1 : 5000. They also investigated the isotopic ratio in hydrogen from freshly prepared electrolytic cells and found it to be about 1 : 25,000. A value distinctly lower than the last three has been found by (Mrs.) E. H. Ingold, C. K. Ingold, H. Whitaker, and R. Whytlaw-Gray,[39] who, by the action of metals on water and by electrolysis, have prepared specimens of water containing a low proportion of deuterium and have compared their densities with that of standard water by using a delicate float method. The value given in a preliminary notice is 1 : 9000.

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[29] *Op. cit.*, p. 100.

[30] *Physical Rev.*, 1933, **43**, 103; *A.*, 1933, 203.

[31] H. D. Babcock, *ibid.*, 1929, **34**, 540; *A.*, 1929, 971; 1930, 1232.

[32] R. Mecke and W. H. J. Childs, *Z. Physik*, 1931, **68**, 362; *A.*, 1931, 543; see also S. M. Naudé, *Physical Rev.*, 1930, **36**, 333; H. M. Kallmann and W. Lasareff, *Z. Physik*, 1933, **80**, 237; *A.*, 1933, 333; R. T. Birge and D. H. Menzel, *Physical Rev.*, 1931, [ii], 37, 1669; *A.*, 1933, 204; F. W. Aston, *Nature*, 1932, **130**, 21.

[33] *Physical Rev.*, 1932, **41**, 32.

[34] *Naturwiss.*, 1932, **20**, 206.

[35] *Physical Rev.*, 1933, **43**, 672.

[36] *J. Amer. Chem. Soc.*, 1933, **55**, 1297.

[37] *J. Chem. Physics*, 1933, **1**, 341.

[38] *Physical Rev.*, 1933, **44**, 265; *A.*, 1933, 994.

[39] *Nature*, 1934, **134**, 661.

If, now, we calculate the atomic weight of hydrogen on the chemical scale, using the two extreme values for the isotopic ratio, *viz.*, D : H = 1 : 5000 and 1 : 9000, we get respectively 1·00776 and 1·00767, both of which are smaller than the mean value found by chemical methods, *viz.*, 1·00777, which should itself be less than the true value.

H. Muckenthaler,[40] in an interesting paper, has fully discussed this discrepancy, and contends that it is to be explained by the use of an erroneous value for the isotopic ratio in oxygen. He has redetermined this ratio, using (Sir) J. J. Thompson's parabola method, and finds $O^{18} : O^{16} = 1 : 1058$, which lies nearer to the early value of Babcock than to that of Mecke and Childs. It may be noted, however, that, even if we assume Babcock's value for the oxygen ratio, and that of Bleakney and Gould for the proportion of the hydrogen isotopes, the value for hydrogen is only raised to 1·00787, which exceeds the mean chemical value by only 1 part in 10,000. It is evident, then, that there is an unexplained discrepancy between the chemical and the physical value for the atomic weight of hydrogen, and that further work on the chemical side is desirable. R. W.-G.

2. METALLIC CARBONYL AND NITROSYL COMPOUNDS.

A particularly interesting chapter in inorganic chemistry deals with the metallic carbonyl and nitrosyl compounds. Notable advances have been made in our knowledge of these compounds during recent years through the numerous investigations of W. Hieber and W. Manchot and their collaborators. At the present time, amongst the simple carbonyls of the transition elements, five monometallic derivatives are known: $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$, $Mo(CO)_6$, $W(CO)_6$. In 1921, I. Langmuir[1] suggested that the volatile carbonyls represent a type in which the metal atom takes on the number of electrons necessary to reach the atomic number of the next inert gas, nickel adding eight in $Ni(CO)_4$, iron ten in $Fe(CO)_5$, and molybdenum twelve in $Mo(CO)_6$. This implies that each carbon monoxide molecule contributes two electrons to the central metallic atom. It will be noted that this principle applies equally well to the more recently prepared carbonyls of chromium[2] and tungsten.[3] Moreover, it indicates why monometallic carbonyls are not formed by elements of odd atomic number such as cobalt (at. no. 27). It is well known that cobalt carbonyls show a great tendency to polymerise, so that the tetracarbonyl is really $Co_2(CO)_8$,[4] whilst the tricarbonyl gives a molecular weight in $Fe(CO)_5$ which indicates the complexity $Co_4(CO)_{12}$.[5]

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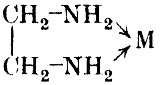
[40] *Physikal. Z.*, 1934, **35**, 851; *A.*, 1283.

[1] *Science*, 1921, **54**, 65; *A.*, 1922, ii, 137.

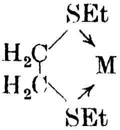
[2] A. Job and A. Cassal, *Compt. rend.*, 1926, **183**, 392; *A.*, 1926, 1017; *Bull. Soc. chim.*, 1927, **41**, 1041; M. M. Windsor and A. A. Blanchard, *J. Amer. Chem. Soc.*, 1934, **56**, 823; *A.*, 589.

[3] A. Job and J. Rouvillois, *Compt. rend.*, 1928, **187**, 564; *A.*, 1928, 1201.

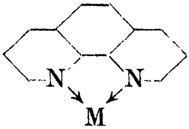
Recent work has fully established that the carbon monoxide molecule can be substituted by other molecules, with the production of new substances of great theoretical interest. For example, one such group may be substituted by a molecule of ammonia, pyridine (py), or alcohol, and two groups by chelate groups such as ethylenediamine (en) (I), the diethyl ether of dithioglycol (th) (II), or *o*-phenanthroline (phen) (III). In this way such substances are produced as



(I.)



(II.)



(III.)

$Cr(CO)_3py_3$,[6] $Fe(CO)_3(NH_3)_2$, $Ni(CO)_2phen$,[5] $Fe_2(CO)_5en_2$.[7] It will be seen that in all these cases the covalency of the metal is the same as in the simple carbonyls from which they are derived. A second series arises by an alteration in the covalency of the metallic atom. The most remarkable examples of this type are iron carbonyl hydrogen and cobalt carbonyl hydrogen and their derivatives. The volatile $Fe(CO)_4H_2$ [8] is an unstable yellow liquid (m. p. — 70°) formed by the action of alkalis on iron pentacarbonyl : $Fe(CO)_5 + 2OH' = Fe(CO)_4H_2 + CO_3''$. The extreme ease of oxidation of the coordinately bound carbonyl group in alkaline medium is a distinctive feature of the reaction. Methylene-blue is quantitatively reduced by $Fe(CO)_4H_2$, and the active hydrogen may be determined in this way. An outstanding property of this carbonyl hydride is the ability to form salts with organic bases such as pyridine and *o*-phenanthroline, whereby the stable compounds $Fe(CO)_4H_2,(C_5H_5N)_x$ and $Fe(CO)_4H_2,2C_{12}H_8N_2$ are produced. The hydrogen in the latter compound no longer reduces methylene-blue.

In appropriate non-aqueous solvents, iron pentacarbonyl reacts with halogens to give $Fe(CO)_4X_2$[9] where $X = Cl$, Br, or I; whilst with mercuric sulphate in sulphuric acid solution, the pentacarbonyl yields $Fe(CO)_4Hg$.[10] Other members of this series[11] which are regarded as salts of $Fe(CO)_4H_2$ include $Fe(CO)_4Na_2$, $Fe(CO)_4Cd$, $[Fe(CO)_4H]_2,[Ni(NH_3)_6]$, for dilute mineral acids liberate $Fe(CO)_4H_2$ from them. Similar investigations with the other metallic carbonyls gave positive results only in the case of cobalt carbonyls. It has been known for some time that the following reaction is realisable :

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[4] L. Mond, H. Hirtz, and M. D. Cowap, *J.*, 1910, **97**, 798.

[5] W. Hieber, F. Mühlbauer, and E. A. Ehmann, *Ber.*, 1932, **65**, [*B*], 1090; *A.*, 1932, 920.

[6] W. Hieber, *Sitzungsber. Heidelberg. Akad. Wiss.*, 1929, **3**, 4.

[7] W. Hieber and F. Sonnekalb, *Ber.*, 1928, **61**, 558; *A.*, 1928, 510.

[8] W. Hieber and F. Leutert, *Naturwiss.*, 1931, **19**, 360; *A.*, 1931, 810; W. Hieber and H. Vetter, *Ber.*, 1931, **64**, [*B*], 2340; *A.*, 1931, 1255; *idem*, *Z. anorg. Chem.*, 1933, **212**, 145; *A.*, 1933, 685.

$$2Co(CO)_3M + 2H^{\cdot} = Co^{\cdot\cdot} + Co(CO)_4H + 2CO + \tfrac{1}{2}H_2 + M$$

(M = alcohol or amine constituent.)

Quite recently, however, E. A. Ehmann[12] has stated that if the reaction with $Co(CO)_4$ is carried out in an aqueous solution of alkali or baryta, a similar result is obtained to that with $Fe(CO)_5$, but the mechanism is more complicated :

$$3Co(CO)_4 + 2OH' = 2Co(CO)_4H + CO_3'' + Co(CO)_3 \text{ (polymerised).}$$

A part of the tetracarbonyl is decomposed simultaneously with liberation of carbon monoxide but without hydrogen evolution :

$$3Co(CO)_4 + 2H_2O = 2Co(CO)_4H + Co(OH)_2 + 4CO.$$

The presence of $Co(CO)_4H$ was proved by oxidation with hydrogen peroxide, as well as by titration with methylene-blue. Although the isolation of such salts as $[Co(CO)_4]_2[Ni(NH_3)_6]$ and $[Co(CO)_4]_2[Co(phen)_3]$ confirms the formula for the parent hydride, this has not yet been obtained. In chemical behaviour, the carbonyl hydride of cobalt is distinguished from that of iron by its much greater sensitivity; *e.g.*, spontaneous decomposition with formation of free carbonyl and free hydrogen occurs rapidly in acid solution at the ordinary temperature. It is significant that, so far, no hydride of nickel carbonyl has been obtained, nor any salt derived from it. Examination of the following series shows that the E.A.N.* of the metal is in each case that of the next inert gas : $Fe(CO)_5$, $Fe(CO)_4H_2$, $Co(CO)_4H$, $Ni(CO)_4$.

Lastly, reference must be made to the interesting series of changes that occur when the carbonyls react with nitric oxide. From the reaction of this gas and $Fe(CO)_4$ dissolved in $Fe(CO)_5$, a red crystalline compound $Fe(CO)_2(NO)_2$ (m. p. 18·5°) is obtained which decomposes at 70°.[13] Under appropriate conditions, this nitrosocarbonyl reacts with iodine, pyridine, or *o*-phenanthroline to give $Fe(NO)_2I$, $Fe_2(NO)_4(py)_3$, and $Fe(NO)_2phen$.[14] When iron pentacarbonyl is heated with nitric oxide under pressure, black crystals of iron tetranitrosyl, $Fe(NO)_4$, are obtained.[14] Similar reactions are recorded with cobalt carbonyls. Slowly at room temperature, instantaneously at 40°, nitric oxide reacts with $Co(CO)_4$ to form a cherry-red liquid (b. p. 78·6°) having the molecular formula $Co(CO)_3NO$. With pyridine, this cobalt nitrosocarbonyl yields $Co_2(NO)_2CO,2py$, and with *o*-phenanthroline, in benzene or methyl alcohol, the complex substance $CoNO(CO)_2,C_{12}H_8N_2$.[14] Other results of great interest have been omitted from this account, but sufficient has been recorded to indicate the substantial achievements in this field of research.

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[9] W. Hieber and G. Bader, *Ber.*, 1928, **61**, [*B*], 1717; *A.*, 1928, 1202.

[10] H. Hock and H. Stuhlmann, *Ber.*, 1929, **62**, [*B*], 431, 2690; *A.*, 1929, 412; 1930, 47.

[11] F. Feigl and P. Krumholz, *Z. anorg. Chem.*, 1933, **215**, 242; *A.*, 1934, 159.

[12] See W. Hieber, *Z. Elektrochem.*, 1934, **40**, 158; *A.*, 617.

* E.A.N. = effective atomic number, *i.e.*, total number of electrons, shared and unshared (see N. V. Sidgwick, " Electronic Theory of Valency," 1927, p. 163).

The constitution of the metallic carbonyl and nitrosyl compounds is a fascinating but difficult problem. It cannot be said that a final decision has yet been reached, but an important paper by N. V. Sidgwick and R. W. Bailey [15] places the structures of these compounds on a much firmer basis. The experimental work already reviewed shows that, in the carbonyls, a carbon monoxide group occupies one co-ordination position and thereby provides two electrons to form a link with the metallic atom. The carbon monoxide molecule is obviously capable of co-ordinating through either the carbon or the oxygen atom, but Sidgwick and Bailey consider that it is more probable that the link is formed through the carbon, thus $M \leftarrow CO$, since the 4-covalent condition is the normal state of the carbon atom whereas it only rarely occurs with oxygen [*e.g.*, in basic beryllium acetate, $Be_4O(CH_3{\cdot}CO{\cdot}O)_6$]. They further state that carbon monoxide is correctly formulated as $:C\underset{\times\times}{\overset{\cdot\cdot}{}}\underset{\times}{\overset{\times}{}}O\underset{\times}{\overset{\times}{}}$ or $\overset{-}{C}\equiv\overset{+}{O}$. This formula, originally proposed by I. Langmuir,[16] has been shown by D. L. Hammick, R. G. A. New, N. V. Sidgwick, and L. E. Sutton [17] to be supported by the electrical dipole moment, the interatomic distance, the heat of formation, the force constant, and the parachor. N. V. Sidgwick [18] has emphasised that the minute moment (0·12) of carbon monoxide can be explained only by supposing that the very unequal sharing of electrons between the carbon and oxygen is offset by the transference of an electron from the oxygen to the carbon. The observation of L. E. Sutton and J. B. Bentley,[19] that the electrical dipole moment of nickel carbonyl is zero, strongly supports the idea of a triple bond between the carbon and oxygen, whilst the Raman spectrum of nickel carbonyl [20] confirms the presence in it of a triple link of carbon to oxygen. Nevertheless, objections to this formulation have been raised recently by R. Samuel and his collaborators.[21] They conclude that the evidence from molecular spectra and considerations of wave-mechanics favour the classical formula $\mathrm{C{=}O}$; their arguments, however, are based on an interpretation of molecular spectra which disagrees with those of W. Heitler and F. London, of L. Pauling, and of J. E. Lennard-Jones. Much more important arguments are brought forward by L. Pauling,[22] who concludes that carbon monoxide is in resonance between the two forms $\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$ and $\mathrm{C{=}O}$, with the former predominating. The resonance would explain why the length and heat of rupture of the link are those required by the triple link; it would also justify the use of the triple link as the normal structure. There is, therefore, a very strong case for the view that the triple-bonded structure predominates in carbon monoxide and that the monometallic carbonyls are correctly written as $\mathrm{M}\leftarrow\overset{-}{\mathrm{C}}\equiv\overset{+}{\mathrm{O}}$ or $\overset{-}{\mathrm{M}}-\mathrm{C}\equiv\overset{+}{\mathrm{O}}$. Sidgwick and Bailey have pointed out a curious regularity in the composition of the carbonyls, whether they contain one or more metallic atoms in the molecule. If we calculate the E.A.N. of the metallic atoms by adding 2 to the atomic number of the metal for each carbonyl group, then the difference between the result and the atomic number of the next inert gas is always one less than the number of metallic atoms in the molecule. For a molecule $\mathrm{M}_x(\mathrm{CO})_y$, the equation $G - \frac{1}{x}(xm + 2y) = x - 1$ is always true, where m is the atomic number of M and G that of the next inert gas. When $x = 1$ (monometallic), this, as we have seen, holds in every case. It also holds with all the polymetallic carbonyls known: $\mathrm{Fe_2(CO)_9}$, $\mathrm{Fe_3(CO)_{12}}$, $\mathrm{Co_2(CO)_8}$, and $\mathrm{Co_4(CO)_{12}}$. In these, the molecule must be held together by further co-ordination, obviously through the oxygen as donor, $\overset{-}{\mathrm{M}}-\overset{+}{\mathrm{C}}\equiv\overset{+}{\mathrm{O}}-\overset{-}{\mathrm{M}}$, every such link involving the sharing of two more electrons. If we may assume that, as in the simple carbonyls, this leads to each metallic atom in the polymetallic carbonyls having the E.A.N. of the inert gas, it follows from the equation that the number of such new links through the oxygen must be 1 when $x = 2$, 3 when $x = 3$, and 6 when $x = 4$. This implies that the molecules in question are respectively linear, triangular, and tetrahedral, as shown in Figs. 1, 2, and 3. The crystal structures of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ have been examined by R. Brill,[23] and are compatible with the configurations proposed. The fact that these two substances are diamagnetic, like $Fe(CO)_5$ and $Ni(CO)_4$, is held to support these assumptions.

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[13] W. Hieber and J. S. Anderson, *Z. anorg. Chem.*, 1932, **208**, 238; *A.*, 1932, 1219.

[14] *Idem*, *ibid.*, 1933, **211**, 132; *A.*, 1933, 476.

[15] *Proc. Roy. Soc.*, 1934, [*A*], **144**, 521; *A.*, 833.

[16] *J. Amer. Chem. Soc.*, 1919, **41**, 1543; *A.*, 1919, ii, 506.

[17] *J.*, 1930, 1876; *A.*, 1930, 1239; see also N. V. Sidgwick, *Chem. Reviews*, 1931, **9**, 77.

[18] See N. V. Sidgwick, "The Covalent Link," 1933, p. 187.

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[19] *Nature*, 1932, **130**, 314; *A.*, 1932, 1077; L. E. Sutton, R. G. A. New, and J. B. Bentley, *J.*, 1933, 652; *A.*, 1933, 765.

[20] J. S. Anderson, *Nature*, 1932, **130**, 1002; *A.*, 1933, 113.

[21] H. Lessheim and R. Samuel, *Proc. Physical Soc.*, 1934, **46**, 523; *A.*, 945; R. F. Hunter and R. Samuel, *J.*, 1934, 1180; *A.*, 1058; *Nature*, 1934, **134**, 971.

[22] *J. Amer. Chem. Soc.*, 1932, **54**, 988; *A.*, 1932, 561.

FIG. 1.—$Fe_2(CO)_9$.

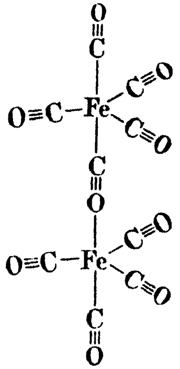
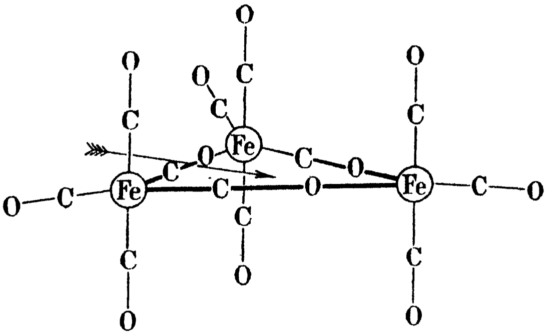


FIG. 2.—$Fe_3(CO)_{12}$.



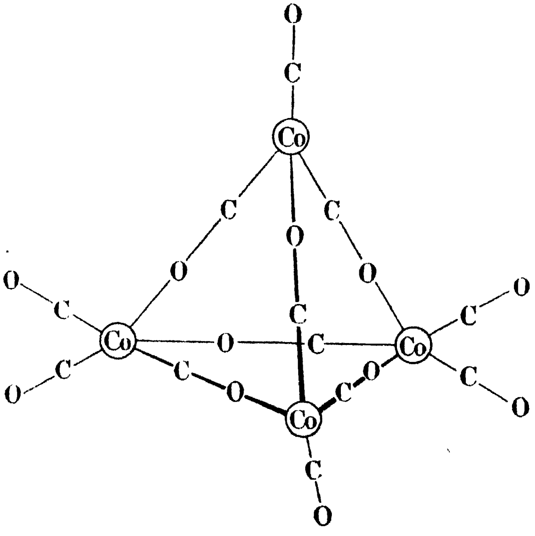


FIG. 3.—$Co_4(CO)_{12}$.

In their preparation and properties, the nitrosyl compounds show a close analogy to the carbonyls. They are commonly formed by the same metals and may be prepared by the direct action of nitric oxide, like the carbonyls by that of carbon monoxide. It has been suggested that the nitrosyls are derivatives of hyponitrous acid $\mathrm{OH{\cdot}N{:}N{\cdot}OH}$, but there is substantial evidence against such an idea. Nitrosyl compounds are formed from nitric oxide and not from hyponitrous acid (except under conditions where the latter forms nitric oxide). Again, hyponitrites in the presence of acids yield nitrous oxide, whereas nitrosyls readily liberate nitric oxide with acids, just as the carbonyls liberate carbon monoxide. Moreover, those compounds containing one NO group to one metallic atom, such as the nitroprussides, would require a formula double the accepted one. There is no evidence in favour of this and much against it. It can scarcely be doubted that each NO group is separately attached to the metal. The great similarity between the nitrosyls and the carbonyls suggests that their structures are very similar and that there is a triple bond between the nitrogen and oxygen, giving $\mathrm{M{-}N{\equiv}O}$, corresponding to $\mathrm{M{-}C{\equiv}O}$. The structure of nitric oxide must, however, differ from that of carbon monoxide, for nitrogen has one more electron than carbon. Now it is known that the $[\mathrm{NO}]^{\cdot}$ ion can exist in polar compounds such as $[\mathrm{NO}]\mathrm{ClO_4}$,[24] $[\mathrm{NO}]\mathrm{SO_4H}$,[24] and $[\mathrm{NO}]\mathrm{BF_4}$,[25] and N. V. Sidgwick and R. W. Bailey assume that the NO group, like the carbon monoxide molecule, is attached to the metal by a link of two shared electrons, but that, in addition, it transfers a further electron and thereby counts as three towards the E.A.N. of the metal. The suggestion that NO contributes three electrons to the E.A.N. of the metallic atom has been made already by other observers but the detailed mechanism of the linkage has not previously been discussed. The structures proposed are $[\dot{:}\mathrm{N}\underset{\times\times\times}{\overset{\cdot\cdot}{}}\overset{\times}{\underset{\times}{}}\mathrm{O}\overset{\times}{\underset{\times}{}}]^{+}$, $\mathrm{N}\equiv\overset{+}{\mathrm{O}}$, $\overset{=}{\mathrm{M}}-\overset{+}{\mathrm{N}}\equiv\overset{+}{\mathrm{O}}$. Support for this theory is forthcoming in the simple cases of the carbonyl and nitrosyl compounds of copper. The former[26] are all of the type $\mathrm{Cu(CO)Br}$, where the copper is cuprous, but their nitrosyl[27] analogues are derived from cupric copper, *e.g.*, $\mathrm{Cu(NO)Cl_2}$ and $\mathrm{Cu(NO)SO_4}$. The extra electron contributed by the NO group to the copper satisfactorily explains this distinction. Although there is no ferric analogue of the complex compound

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[23] *Z. Krist.*, 1927, **65**, 85; 1931, **77**, 36; *A.*, 1928, 108; 1931, 671.

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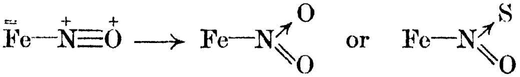
[24] A. Hantzsch and K. Berger, *Z. anorg. Chem.*, 1930, **190**, 321; *A.*, 1930, 1007.

[25] E. Wilke-Dörfurt and G. Balz, *ibid.*, 1927, **159**, 197; *A.*, 1927, 120.

[26] O. H. Wagner, *ibid.*, 1931, **196**, 364; *A.*, 1931, 581.

[27] W. Manchot, *Annalen*, 1910, **375**, 308; *A.*, 1910, ii, 956; *Ber.*, 1914, **47**, 1601; *A.*, 1914, ii, 567; W. Manchot and E. Linckh, *ibid.*, 1926, **59**, 407; *A.*, 1926, 452.

$M_3[Fe(CN)_5CO]$, it is notable that ferric derivatives of this type, when they do occur, have the corresponding more stable ferrous analogues. It is surprising, therefore, that if iron be considered as ferric in the nitroprussides $M_2[Fe(CN)_5NO]$ no ferrous equivalent is available. However, the theory of the NO linkage advanced by Sidgwick and Bailey removes this anomaly, for on their interpretation the iron is ferrous in the nitroprussides. Their explanation of the colour reactions of the nitroprussides is particularly interesting. It is well known that reaction does not occur with hydrogen sulphide, but addition of alkali or alkaline sulphide to the solution produces the deep purple colour of $M_4[Fe(CN)_5(NOS)]$.[28] Again, hydroxyl ions convert nitroprussides into nitro-compounds, $M_4[Fe(CN)_5(NO_2)]$.[29] It is considered that the strongly positive $\overset{+}{N}\equiv\overset{+}{O}$ group attracts the negative OH′ or S″ (or HS′) ions with the production of a nitro- or thionitro-group :



The method of formulation adopted by Sidgwick and Bailey for nitrosyl compounds leads to the maintenance of the inert-gas rule in the majority of cases, even in such complicated molecules as those of Roussin's "red and black salts," $KFe_4(NO)_7S_3$ and $K_2Fe_2(NO)_4S_2$.

Closely allied to the compounds just discussed are nickel derivatives of the type NiSR,NO and the related iron and cobalt compounds MSR,2NO. Special importance is attached to these substances, for W. Manchot and his collaborators, who systematically studied them, consider that the metal atoms exhibit univalency. Before accepting this conclusion, however, it is profitable to examine it in detail. It is obviously arrived at by considering merely the so-called principal valency of the atom in the sense of Werner's theory, and neglecting the influence of the NO group. This naturally raises the important question as to what is meant by the absolute valency of an atom in compounds of this type. A definition which will be universally applicable is not easy to formulate, but on the whole, the best seems to be that of H. G. Grimm and A. Sommerfeld,[30] who consider that the absolute valency of an atom is numerically equal to the number of electrons of the atom "engaged" in attaching the other atoms. Now, according to Sidgwick and

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[28] J. F. Virgili, *Z. anal. Chem.*, 1906, **45**, 409; *A.*, 1906, i, 637.

[29] L. Cambi and L. Szegö, *Atti R. Accad. Lincei*, 1927, **5**, 737; *A.*, 1927, 917; *Gazzetta*, 1928, **58**, 71; *A.*, 1928, 345.

[30] H. G. Grimm and A. Sommerfeld, *Z. Physik*, 1926, **36**, 36; *A.*, 1926, 560. See also N. V. Sidgwick, "The Electronic Theory of Valency," p. 182.

Bailey's theory, NiSR,NO should have the structure $\overset{+}{O}\equiv\overset{+}{N}-\overset{=}{Ni}-SR$, so that the nickel atom has as many unshared electrons as the isolated nickel atom and hence the valency of the nickel is zero. This is one of the absurdities to which the system of Grimm and Sommerfeld occasionally leads, but it does emphasise the difficulty of assigning to the metal atom in these compounds a numerical value of absolute valency. There is, of course, no doubt about the existence of compounds of univalent nickel, as the isolation of $K_2Ni(CN)_3$ has shown, but the series under consideration are only correctly designated derivatives of univalent iron, cobalt, and nickel in the restricted sense of Werner's principal valency. In the appended table, the nitrosyl compounds under discussion are summarised.[31]

	Type MSR,2NO.	Type MSR,NO.
FeSK,2NO	FeS_2O_3K,2NO	NiSEt,NO
Fe_4S_3K,7NO	$[Fe(S_2O_3)_2]K_3$,2NO	NiSPh,NO
FeSEt,2NO	CoSEt,2NO	NiSPh,NO,py
FeSPh,2NO	CoSPh,2NO	$[Ni(S_2O_3)_2]K_3$,NO
	$[Co(S_2O_3)_2]K_3$,2NO	

The mechanism of the reduction to the univalent stage in the case of the simple mercaptides is very interesting. The nickel mercaptide $Ni(SEt)_2$, for example, forms the unstable intermediate product $Ni(SEt)_2$,2NO, which loses nitrosyl mercaptide, NO·SEt, in accordance with the equations

$$(1)\ Ni(SEt)_2 + 2NO = Ni(SEt)_2,2NO$$
$$(2)\ Ni(SEt)_2,2NO = NiSEt,NO + NOSEt$$

Depending on experimental conditions, the NOSEt undergoes more or less rapid decomposition into disulphide and nitric oxide :

$$(3)\ 2NOSEt = 2NO + EtS{\cdot}SEt.$$

By similar reactions, ferrous and cobaltous mercaptides yield the complex compounds FeSEt,2NO and CoSEt,2NO.[32] These derivatives are covalent, for they dissolve in organic solvents and have low melting points (polar compounds would have appreciably higher melting points). Their intense colours are attributed to the deformation of the nitric oxide molecule on the basis of Fajans's theory.

The complex thiosulphates are obtained when metallic salts, *e.g.*, nickel chloride or cobaltous acetate, react with nitric oxide in presence of excess of sodium thiosulphate. The nickel salt, $K_3[Ni(S_2O_3)_2NO],2H_2O$, is fairly stable, but potassium cyanide[33] converts it into the less stable complex cyanide, $K_2[Ni(CN)_3NO]$, which shows the characteristic reactions associated with univalency of the nickel, *viz.*, pronounced reducing properties and liberation of hydrogen from water. This complex cyanide may also be prepared by (*a*) the reaction between nitric oxide and $K_2[Ni(CN)_3]$[33] or (*b*) the replacement of carbon monoxide in the complex compound $K_2[Ni(CN)_3CO]$[34] by nitric oxide.[35] It is possible to convert the ionised compound $K_2[Ni(CN)_3NO]$ into the covalent $Ni(CO)_4$. This is done by addition of acid, which gives the very readily oxidised nickel monocyanide NiCN, which in turn absorbs carbon monoxide to form the unstable intermediate product $(NiCN,CO)_x$,[34] which then decomposes into $Ni(CN)_2$ and $Ni(CO)_4$. W. Manchot and H. Gall[36] have suggested an ingenious process for obtaining nickel carbonyl, based on the above considerations. The process consists in having a carrier, barium sulphate, associated with a nickel salt which is first transformed into a hydrosulphide by hydrogen sulphide. By the action of carbon monoxide on this nickel hydrosulphide, an unstable intermediate compound of univalent nickel is formed which produces $Ni(CO)_4$ in good yield :

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[31] See H. Schmid, *Angew. Chem.*, 1933, **46**, 691; *A.*, 14, for detailed references.

[32] W. Manchot and S. Davidson, *Ber.*, 1929, **62**, 684; W. Manchot and H. Gall, *Ber.*, 1927, **60**, 2318; 1928, **61**, 2393; *A.*, 1928, 35; W. Manchot and F. Kaess, *ibid.*, 1927, **60**, 2175; *A.*, 1927, 1157.

$$2Ni(SH)_2 + 2xCO = 2NiSH(CO)_x + H_2S_2$$
$$2NiSH(CO)_x = Ni(SH)_2 + Ni(CO)_4 + (2x - 4)CO$$

W. W.

3. Molecular Structures.

The publication of A. Stock's Cornell lectures[1] on the hydrides of boron and silicon again focuses attention on a remarkable series of investigations which has clarified the chemistry of this very difficult subject. Included in the volume is a summary of the contents of 69 papers by the author and his co-workers and 15 by other investigators. An important chapter deals with the structures of the boron hydrides. These compounds were formerly prepared by the reaction of hydrochloric acid with the so-called " magnesium boride " made from magnesium and boron trioxide. In 1930 B. D. Steele and J. E. Mills[2] found, in their experiments with aluminium and cerium borides, that the yield of hydrides was better if phosphoric was used instead of hydrochloric acid; and A. Stock[3] has since found that from "magnesium boride," too, a distinctly better yield (11% instead of 4—5%) is obtained with 8*N*-phosphoric acid. Silicon hydrides are generally present in the crude gas, but if beryllium boride,[4] prepared from boron trioxide and silicon-free beryllium, is used instead of "magnesium boride," this contamination can be avoided. The boron hydrides, belong to two series : (1) B_nH_{n+4} : B_2H_6, B_5H_9, B_6H_{10}, $B_{10}H_{14}$; (2) B_nH_{n+6} : B_4H_{10}, B_5H_{11}, and perhaps B_6H_{12}. This is no mere formal classification. The boranes, B_nH_{n+4}, are more stable and have relatively high melting points; the lower members form stable salts with ammonia. The hydroboranes, B_nH_{n+6}, on the other hand, dissociate much more rapidly and melt at considerably lower temperatures than the boranes; their ammonia compounds dissociate even at room temperature. The hydrides separated from the crude condensate include B_4H_{10} (b. p. 18°), B_5H_9 and B_6H_{10} (liquids), and $B_{10}H_{14}$ (m. p. *ca.* 100°). Other hydrides, B_2H_6, B_5H_9 (liquid), and perhaps B_6H_{12}, are obtained by heating B_4H_{10}. No hydride whose molecule contains one or three atoms of boron is at present known. The most important hydride B_2H_6 cannot be prepared directly from a boride and acid, for it is decomposed by water : $B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$. Recently, however, A. B. Burg and H. I. Schlesinger [5] have discovered a new method of preparing it. They subject a current of hydrogen mixed with gaseous boron trichloride, at reduced pressure, to a high-tension electric discharge. In addition to hydrogen chloride, boron, solid hydrides of boron, and some B_2H_6, much B_2H_5Cl is produced, which, on standing, dissociates rapidly into B_2H_6 and BCl_3. A. Stock and W. Sütterlin [6] are of opinion that better results are obtained by using the tribromide instead of the trichloride. By the reaction of B_2H_6 and methyl alcohol,[7] the interesting substance dimethoxyborine (m. p. −130·6°) is produced, $4MeOH + B_2H_6 = 2BH(OMe)_2 + 4H_2$, accompanied by an unstable by-product, possibly a polymeride of BH_2OMe. Water rapidly decomposes dimethoxyborine : $BH(OMe)_2 + 3H_2O = B(OH)_3 + 2MeOH + H_2$.

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[33] W. Manchot, *Ber.*, 1926, **59**, 2445; *A.*, 1927, 33.

[34] W. Manchot and H. Gall, *ibid.*, p. 1060; *A.*, 1926, 698.

[35] Schuler, *Diss.*, T. M. München, 1928.

[36] *Ber.*, 1929, **62**, 678; *A.*, 1929, 526; D.R.-P., 577,144.

[1] The George Fisher Baker Non-resident Lecturership in Chemistry at Cornell University, Cornell University Press, 1933.

[2] *J.*, 1930, 74; *A.*, 1930, 437.

[3] *Op. cit.*, p. 43.

The structure of B_2H_6 is a perpetual puzzle, and in spite of the great ingenuity displayed by numerous writers, it appears that no completely satisfactory solution has yet been reached. The most important reagent for diagnosing the structure of the boron hydrides is ammonia. This forms a series of salts such as $B_2H_6,2NH_3$,[8] $B_4H_{10},4NH_3$,[9] $B_5H_9,4NH_3$,[10] and $B_{10}H_{14},6NH_3$,[10] and their existence is interpreted as indicating the presence of a proportion of atoms of acidic hydrogen in the hydrides. Substitution products may be formed by electrolysis of the boron hydrides [11] in liquid ammonia. When thus electrolysed, B_2H_6 has a conductivity which is considered to be due to the diammine $B_2H_6,2NH_3$ acting as the salt $[B_2H_4](NH_4)_2$. By a secondary reaction, the ions $[B_2H_4]''$ and $[NH_4]^{\cdot}$ yield hydrogen and B_2H_5,NH_2, which still can form a salt $(NH_4)_2[B_2H_3{\cdot}NH_2]$. Electrolysis of this substance gives hydrogen and $B_2H_4(NH_2)_2$. The unsaturated character of the boron hydrides is indicated by the observation that two atoms of sodium may be added to B_2H_6 [8] and B_4H_{10}.[9] The above results are explained by assigning to B_2H_6 and its derivatives the formulæ : [12]

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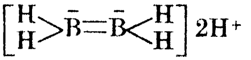
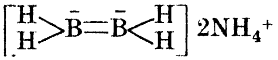
[4] *Op. cit.*, p. 48.

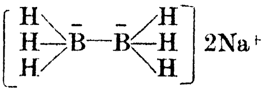
[5] *J. Amer. Chem. Soc.*, 1931, **53**, 4321; *A.*, 1932, 350; A. Stock, H. Martini, and W. Sütterlin, *Ber.*, 1934, **67**, [*B*], 396; *A.*, 497.

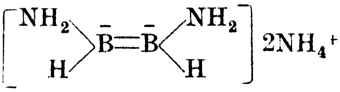
[6] *Ibid.*, p. 407; *A.*, 497.

[7] A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1933, **55**, 4009, 4020; *A.*, 1933, 1257.

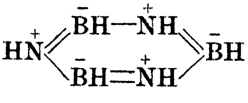








Higher homologues of this series may be similarly formulated. In support of these formulæ it is mentioned [13] that the ultra-violet absorption spectrum of B_2H_6 resembles that of ethylene rather than that of ethane, and that the absorption of B_4H_{10} is similar to that of the conjugated hydrocarbon butadiene, $CH_2{:}CH{\cdot}CH{:}CH_2$. When certain ammonia addition products such as $B_2H_6,2NH_3$ are heated to about 200° for several hours, the exceptionally stable compound $B_3N_3H_6$ [14] is obtained. Its similarity to benzene in certain physical properties has suggested that its structure is probably represented by the inset formula : the double and single bonds can be interchanged exactly as in Kekulé's formula for benzene.



In 1856 J. Nessler proposed the use of an alkaline solution of mercuric iodide and potassium iodide as a reagent for the direct determination of ammonia, and many studies have since been made of the brown compound obtained in this reaction. Some recent observations of M. L. Nichols and C. O. Willits [15] indicate that it has the composition represented by the empirical formula $NH_2{\cdot}Hg_2I_3$. It is very insoluble and tends to separate in very minute particles which are negatively charged and give colloidal solutions. Owing to the agglomeration of the particles, the yellow colour changes to red when ammonia solutions of higher concentration are utilised. This may be prevented, and the colour made permanent over a wide range of ammonia concentrations, by adding a protective colloid, *e.g.*, the addition of 1 c.c. of an 0·5% alkaline ash-free gelatin solution containing 1% of perhydrol to 50 c.c. of Nessler solution.

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[8] A. Stock and E. Pohland, *Ber.*, 1926, **59**, [*B*], 2210; *A.*, 1926, 1217.

[9] A. Stock, E. Wiberg, and H. Martini, *Ber.*, 1930, **63**, 2927; *A.*, 1931, 50.

[10] A. Stock and E. Pohland, *Ber.*, 1929, **62**, 90; *A.*, 1929, 279.

[11] *Op. cit.*, Chap. 21.

[12] E. Wiberg, *Z. anorg. Chem.*, 1928, **173**, 199; *A.*, 1928, 936.

[13] *Op. cit.*, Chap. 26.

[14] *Op. cit.*, Chap. 14.

[15] *J. Amer. Chem. Soc.*, 1934, **56**, 769; *A.*, 614.

In connexion with the structure of hydrazoic acid and the azides, some observations by E. C. Franklin [16] are of interest. From his experimental results, he concludes that most of the reactions of hydrazoic acid support the idea that it is an ammononitric acid, $\mathrm{H{-}N{=}N{\equiv}N}$. This linear structure, originally proposed by Thiele, is nowadays more correctly written as $\mathrm{H{-}N{=}N\overset{\rightarrow}{=}N}$. The action of hydrazoic acid on the metals bears a striking resemblance to that of nitric acid. Contrary to the statements of previous investigators, which are reproduced in most text-books, Franklin finds that no hydrogen is evolved when the acid is treated with zinc, iron, manganese, nickel, or copper. The products are metallic azides, nitrogen, ammonia, and small amounts of hydrazine. With magnesium, however, a small amount of hydrogen may be detected, recalling the fact that this metal yields some hydrogen with very dilute nitric acid. Ferrous azide is converted into ferric azide when heated with excess of hydrazoic acid. Potassium azide may be produced by heating a solution of potassium nitrate and potassamide in liquid ammonia: $\mathrm{KONO_2 + 3KNH_2 = KN{=}N{\equiv}N + 3KOH + NH_3}$.

Whilst the chemical evidence indicates a linear structure for the acid and its salts, the results from crystal structures [17] show clearly that this applies also to the ion $\mathrm{[N\overset{\leftarrow}{=}N\overset{\rightarrow}{=}N]}$. Again, N. V. Sidgwick,[18] in discussing the structure of organic azides, concludes that an organic azide is a mixture of two open-chain forms (*a*) and (*b*) in resonance: (*a*) $\mathrm{R{-}N{=}N\overset{\rightarrow}{=}N}$, (*b*) $\mathrm{R{-}N{\leftarrow}N{\equiv}N}$. A fascinating example of the linearity of the arrangement of the nitrogen atoms in the azide group was recently disclosed by an *X*-ray examination of cyanuric triazide, $C_3N_3(N_3)_3$, by (Miss) I. E. Knaggs. (Sir) W. H. Bragg [19] has pointed out that the arrangement bears a resemblance to the arms of the Isle of Man, a row of three nitrogen atoms lying in the position of each leg from knee to ankle.

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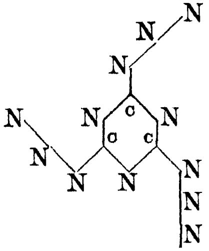
[16] *J. Amer. Chem. Soc.*, 1934, **56**, 568; *A.*, 477.

[17] S. B. Hendricks and L. Pauling, *ibid.*, 1925, **47**, 2904; *A.*, 1926, 113.

[18] *Trans. Faraday Soc.*, 1934, **30**, 801.

[19] *Nature*, 1934, **134**, 138; *A.*, 948.



A number of substances are described in the literature as cadmous compounds, *e.g.*, a sub-halide Cd_4Cl_7 which is supposed to be formed by fusing anhydrous cadmic chloride with metallic cadmium in nitrogen. (Miss) W. R. A. Hollens and J. F. Spencer [20] find that this is really a mixture, for the observed mass susceptibility equals that calculated for the mixture $Cd + 7CdCl_2$. They have also proved that the so-called cadmous hydroxide and oxide prepared from Cd_4Cl_7 are mixtures of cadmium and the corresponding cadmic compound. The relationship between the colour and crystalline structure of precipitated cadmium sulphide has been examined by W. O. Milligan.[21] He infers from his *X*-ray measurements that both the cubic β-CdS and the hexagonal α-CdS may each be yellow or red depending on the conditions of precipitation, and attributes these colour differences to variations in particle size and nature of surface. From the cadmium halides, the α-CdS is the main product, whilst from the sulphate and the nitrate (in hot, acid solution) the β-CdS is obtained.

Some important observations on the so-called calcium sulphate hemihydrate, which is generally recognised as the active principle of plaster of Paris, have been recorded by W. A. Caspari.[22] From solutions of calcium sulphate in hydrochloric, sulphuric, or nitric acid under proper conditions as to dilution of the solvent and temperature, crystals of "hemihydrate" 0·5—1 mm. thick and 3—4 mm. long can be obtained; these belong to the trigonal system, with a density not far below that of anhydrite. In its air-dry condition, the crystal usually contains not more than 4·0—4·5% of water, corresponding rather to $3CaSO_4,H_2O$ than to $2CaSO_4,H_2O$. The moisture content of the "hemihydrate" has been shown by previous investigators, working upon less well-defined materials, to be held in the same way as that of zeolites. Experiments with the trigonal crystals confirm this, for they may be made to give up water to within 0·1% or less of complete dehydration without loss of form or transparency. Exposure to moist air causes the original degree of hydration to be gradually regained. " Dead burning " converts these trigonal crystals into pseudomorphs consisting of ordinary anhydrite. Caspari concludes that anhydrite is apparently dimorphous, there being an orthorhombic, comparatively inert modification, and a trigonal form, stable only up to *ca.* 200°, which can take up water zeolitically. It is the behaviour of the latter form in contact with water that causes plaster to set. The suggestion is made that there may be no essential difference between the " soluble anhydrite " and the " hemihydrate " mentioned in the literature of calcium sulphate.

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[20] *J.*, 1934, 1062; *A.*, 978.

[21] *J. Physical Chem.*, 1934, **38**, 797.

[22] *Nature*, 1934, **133**, 648; *A.*, 720.

The diamond has been studied for a longer period than any other natural stone, and its unique character has always been assumed. It has been left to (Sir) R. Robertson, J. J. Fox, and A. E. Martin [23] to make the fascinating discovery that there are two types of diamond which show striking differences in a number of physical properties, while in other properties no differences whatever can be observed. They find that diamonds showing a laminar structure (I) differ in certain properties from ordinary diamonds (II); the latter have an infra-red absorption band at 8 μ and are opaque to ultra-violet light of less than 3000 Å., whilst (I) have no band at 8 μ and are transparent up to 2250 Å. With (II) the conductivity induced by light is very small, high voltages having to be applied before a current can be detected, whilst (I) give an appreciable current without an applied voltage. Also, (I) are activated by light of 2300 Å., and afterwards give a current in the dark and a large current when re-illuminated with light of more than 5000 Å. These activated diamonds are deactivated by light of 2400—5000 Å. *X*-Ray examination indicates that (I) have a mosaic structure; they are also more optically isotropic than (II), but the specific gravity, refractive index, dielectric constant, and Raman effect are the same for both types. It is considered that the difference between (I) and (II) is not due to impurities, but to different conditions resulting during their formation from the plastic state.

A useful addition to the chemistry of zirconium has been made by M. Picon,[24] who has prepared three definite sulphides, ZrS_2, Zr_3S_5, and Zr_2S_3, of which the last two are new. The method of preparation was to act on zirconium oxide at a high temperature with hydrogen sulphide. By heating first at 1100—1200° and then raising the temperature to 1700°, a fused crystalline mass of

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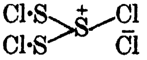
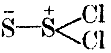
[23] *Phil. Trans.*, 1934, [*A*], **232**, 463; *A.*, 583.

[24] *Compt. rend.*, 1933, **196**, 2003; **197**, 151; *A.*, 1933, 918; *Bull. Soc. chim.*, 1933, [iv], **53**, 1269; *A.*, 1934, 265.

Zr_3S_5 was obtained. On heating this at 900—1300° in hydrogen sulphide, the black ZrS_2 was produced. Brown Zr_2S_3 was formed when Zr_3S_5 was heated at 1400° for 2 hours in a cathode-ray vacuum or at 1700° for one hour in hydrogen. All the products were crystalline. Evidence of the existence of Zr_3S_4 was also obtained. An examination of the chemical properties of these substances indicated that the action of numerous reagents was less pronounced with the compounds containing less sulphur.

The main product of the action of gaseous fluorine on sulphur is the hexafluoride, SF_6, which is a highly stable gas. In addition, two other fluorides S_2F_2 and SF_4 are described in the literature, although N. V. Sidgwick[25] has directed attention to the possibility that SF_4 may not exist. In a recent communication by K. G. Denbigh and R. Whytlaw-Gray,[26] the preparation and properties of a new fluoride, disulphur decafluoride, S_2F_{10}, are described. This very interesting substance was obtained by the fractionation of a large quantity of the hexafluoride. Only small quantities are produced in the reaction of fluorine on sulphur, but the yield is improved by using plastic instead of rhombic sulphur. This new fluoride is stable, but less so than the hexafluoride. Its b. p. is 29°, m. p. −92°, and liquid density 2·08 g./c.c. The parachor is in fair agreement with a sexacovalent structure which, moreover, appears most probable on chemical grounds. The two sulphur atoms are linked together by a single bond, and each sulphur carries five fluorine atoms also linked by single bonds.

Valuable information continues to accumulate about the chlorides of sulphur. For a number of years, T. M. Lowry and his collaborators have been investigating the mechanism of the formation of these compounds. In 1927[27] they discovered that sulphur and chlorine, after being heated in sealed tubes at 100°, gave a product with a freezing-point curve which showed, in addition to the familiar maxima due to the mono- and tetra-chlorides, two well-defined breaks which they attributed to crystallisation of the dichloride and a new chloride S_3Cl_4. Later work demonstrated that the tetrachloride could exist only in the solid state. The fact that the dielectric constant of the solid tetrachloride was much higher than would be expected for anything but a salt led Lowry and G. Jessop[28] to suggest that it is a polar compound; they therefore assigned to the tetrachloride the structure $[\overset{+}{S}Cl_3]\overset{-}{Cl}$, and to the new chloride S_3Cl_4 the configuration  $\begin{matrix}Cl\cdot S\\Cl\cdot S\end{matrix}\!\!>\overset{+}{S}\!-\!\begin{matrix}Cl\\\overset{-}{Cl}\end{matrix}$ or $[\overset{+}{S}_3Cl_3]\overset{-}{Cl}$. The so-called sulphur monochloride, S_2Cl_2, still presented an interesting structural problem, and recently A. H. Spong,[29] in Lowry's laboratory, reviewed the relevant physical data available (*e.g.*, Raman spectrum, parachor, and dielectric properties) and concluded that ordinary sulphur monochloride is probably a mixture of the two forms (1)  $\overset{-}{S}-\overset{+}{S}<\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$ and (2) Cl·S·S·Cl. He has also investigated the reaction between sulphur monochloride and chlorine, which is generally represented by the simple equation $S_2Cl_2 + Cl_2 = 2SCl_2$. It is, however, recognised that the reaction is definitely more complicated than this, and A. H. W. Aten [30] had suggested that it is an autocatalytic reaction, both the di- and the tetra-chloride being active in catalysing the process. A. H. Spong [31] now finds that no effect ascribable to sulphur tetrachloride can be observed, but that the reaction velocity is markedly influenced by the concentration of S_3Cl_4. He considers that the primary mechanism is probably ionic, the chlorine ion attacking the negatively charged sulphur atom in the modification of the monochloride with formula (1). The mechanism he proposes is :

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[25] *Ann. Reports*, 1933, **30**, 126.

[26] *J.*, 1934, 1347.

[27] T. M. Lowry, L. P. McHatton, and G. G. Jones, *J.*, 1927, 746; *A.*, 1927, 505.

[28] *J.*, 1929, 1421; *A.*, 1929, 978; *J.*, 1930, 782; *A.*, 1930, 666.

$$(a)\ S_2Cl_2 + \overset{-}{Cl} = SCl_2 + \overset{-}{S}Cl$$

$$(b)\ \overset{+}{S}_3Cl_3 + \overset{-}{S}Cl = SCl_2 + S_3Cl_2$$

$$(c)\ S_3Cl_2 + Cl_2 = \overset{+}{S}_3Cl_3 + \overset{-}{Cl}.$$

V. Zappi and V. Cortelezzi [32] examine the experimental data which are held to favour polar structures for certain halogen derivatives of the non-metals. The evidence for this possibility in the case of phosphorus pentachloride was very slight; according to A. Voigt and W. Biltz,[33] the compound is entirely non-conducting, and J. H. Simons and G. Jessop support this conclusion.[34] Moreover, these investigators point out that a polar formula is definitely ruled out by their observation that, in carbon tetrachloride, phosphorus pentachloride has zero or a very small dipole moment. The support for a polar structure is the experimental data of G. W. F. Holroyd, H. Chadwick, and J. E. H. Mitchell,[35] who found that the pentachloride had a small conductivity in nitrobenzene but none in benzene and ethylene dibromide. Now Zappi and Cortelezzi conclude from their experiments that such measurements in nitrobenzene are subject to large errors and are unreliable. They find, however, that solutions of phenyl dichloroiodide in carefully purified nitrobenzene and in phosphorus oxychloride show a very feeble electrical conductivity, whilst the cryoscopic molecular weight is low. They contend that this does not indicate that the structure is [PhICl]Cl but that the experimental results may be due to dissociation in accordance with the equation: $PhICl_2 \rightleftarrows PhI + Cl_2$. They also examine critically similar experimental data given by other compounds such as iodine trichloride, and conclude that the feeble conductivities which have been recorded may be more rationally explained as due to the dissociation of complexes formed with the solvent. Cryoscopic dissociation they also regard as molecular and not ionic. The conclusion that phosphorus pentachloride and iodine trichloride are covalent compounds will be generally accepted.

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[29] *J.*, 1934, 485; *A.*, 605.

[30] *Z. physikal. Chem.*, 1905, **54**, 55.

[31] *J.*, 1934, 1283.

[32] *Bull. Soc. chim.*, 1934, [v], **1**, 509.

[33] *Z. anorg. Chem.*, 1924, **133**, 297; *A.*, 1924, ii, 552.

[34] *J. Amer. Chem. Soc.*, 1931, **53**, 1263; *A.*, 1931, 669.

[35] *J.*, 1925, **127**, 2492; *A.*, 1926, 15.

The iodine in periodic acid tends to pass into the 6-covalent state, so that the ordinary periodic acid is $H_5[IO_6]$. The 4-covalent form $H[IO_4]$ has been only once described, but J. R. Partington and R. K. Bahl[36] now show that HIO_4 is a definite compound, although no evidence could be found of the existence of the anhydride I_2O_7 or of mesoperiodic acid H_3IO_5. Periodic acid, H_5IO_6, at 100° in a vacuum loses $2H_2O$ and HIO_4 is formed. On heating at 80° in a vacuum two molecules of H_5IO_6 lose $3H_2O$, $H_4I_2O_9$ being formed.

In general, cupric copper does not readily form 6-co-ordinated compounds, and its covalency is normally 4. It was surprising, therefore, when in 1927 W. Wahl[37] stated that he had prepared a lævorotatory iodide $[Cu(en)_2(H_2O)_2]I_2$ and thus established that 6-covalent copper was of octahedral type. Now, C. H. Johnson and S. A. Bryant[38] have reinvestigated this matter. All their attempts at a resolution were unsuccessful, and moreover, their analyses show that there are no grounds for presuming that the ion $[Cu(en)_2(H_2O)_2]^{\cdot\cdot}$ is present in the crystalline salt. They incline to the view that the constitution of the ion in the crystal is $[Cu(en)_2]^{\cdot\cdot}$, where the covalency of the copper is 4 and not 6, and so optical isomerism cannot arise. Some earlier work of G. T. Morgan and his co-workers lends support to this structure.

The valuable co-ordinating properties of the tridentate group 2 : 2′ : 2″-tripyridyl (trpy) have been applied with success to the problem of the structure of 4-covalent compounds of platinum. G. T. Morgan and F. H. Burstall[39] have succeeded in isolating a red crystalline salt, $[Pt(trpy)Cl]Cl,2$ or $3H_2O$, and thereby provided an elegant chemical proof that in this co-ordination compound the four valencies of the platinum atom must be planar, for a tetrahedral structure is inadmissible. If a model of this molecule (I) is built up on the assumption that the pyridine rings have the Kekulé structure, it will be found that chelation can take place without undue strain only if in two of the pyridine rings the double bonds are fixed, *i.e.*, not oscillating between the two possible Kekulé forms.

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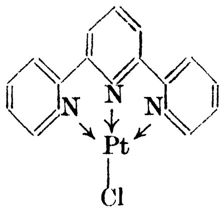
[36] *J.*, 1934, 1088; *A.*, 979.

[37] *Acta Sci. Fennicae Comm. Phys.-Math.*, 1927, **4**, 1; *A.*, 1928, 395; *Ann. Reports*, 1933, **30**, 100.

[38] *J.*, 1934, 1783.

[39] *Ibid.*, p. 1498.

(I.)



F. G. Mann[40] has shown that ββ'-diaminodiethylamine, $(NH_2 \cdot C_2H_4)_2NH$, can act as a tridentate group with platinous salts, but as this triamine may occupy the three points of a triangular face, it is uncertain whether the salt $[BrPt(NH_2 \cdot C_2H_4)_2NH]Br$ is planar or tetrahedral. Further interesting stereochemical questions are raised in a paper by G. T. Morgan and F. H. Burstall[41] dealing with 2 : 2'-dipyridylplatinum salts, and in a communication by J. S. Anderson[42] on Zeise's salt $K[PtCl_3,C_2H_4],H_2O$.

In 1930, F. G. Angell, H. D. K. Drew, and W. Wardlaw[43] brought forward new experimental data about the two known forms of the thio-ether addition compound $(Et_2S)_2PtCl_2$, which indicated that further investigation of this group of substances was necessary as the chemical evidence available did not afford any confirmation of the planar structure. The results of recent chemical and *X*-ray experiments by E. G. Cox, H. Saenger, and W. Wardlaw[44] with the dimethyl sulphide derivatives of platinous and palladous chlorides, $[Pt(Me_2S)_2Cl_2]$ and $[Pd(Me_2S)_2Cl_2]$, prove that the two isomerides of the former are planar *cis-trans*-compounds. The α-form is the *trans*-compound, not the *cis*- as suspected by Werner, and it is not tetrahedral as suggested by others. The *X*-ray results with the β-isomeride are less definite, but it seems likely that the sulphur atoms are in *cis*-positions and that the compound is ionised in the solid state. In the case of the palladous compound, only one form was obtained; this is isomorphous with the α-platinous compound and is therefore the plane *trans*-compound. The chemical reactions of the substances differ very considerably, notably with silver oxide. The β-platinous compound reacts rapidly with this reagent, with production of silver chloride and a basic substance which forms an alkaline solution in water and yields the original substance with acid. The α-form, on the other hand, reacts only slowly, with evolution of dimethyl sulphide and precipitation of platinum as hydroxide or oxide. The so-called third form of $Pt(Me_2S)_2Cl_2$ has been shown by L. Tschugaeff and W. Surbotin [45] to be really the plato-salt, $[Pt(Me_2S)_4][PtCl_4]$, a result confirmed by the present investigators. The diethyl sulphide derivatives of platinous and palladous chlorides have also been submitted to a detailed chemical examination by H. D. K. Drew and G. H. Wyatt,[46] who draw conclusions regarding the structures, substantially in agreement with the results obtained for the dimethyl sulphide derivatives.

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[40] *J.*, 1934, 466; *A.*, 640.

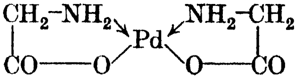
[41] *Ibid.*, p. 965; *A.*, 1113.

[42] *Ibid.*, p. 971; *A.*, 994.

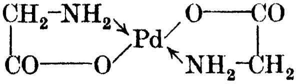
[43] *J.*, 1930, 349; *A.*, 1930, 559.

[44] *J.*, 1934, 182; *A.*, 397.

Palladium, like platinum, has been shown by *X*-ray [47] methods to give planar configurations in certain of its 4-covalent compounds. In no case, however, had the *cis*- and *trans*-isomerism demanded by theory been established. Recently,[48] from the reaction of glycine and potassium chloropalladite, two substances were isolated, *viz.*, yellow prisms, $Pd(NH_2{\cdot}CH_2{\cdot}CO_2)_2,3H_2O$, and glistening, light yellow, anhydrous plates. These have been shown by *X*-ray and chemical experiments to be different in structure and to have the *cis-trans*-planar configurations



and



A. A. Grünberg and V. M. Schulman [49] have also described two forms of $Pd(NH_3)_2Cl_2$ which they consider to be *cis*- and *trans*-isomerides.

W. W.

4. SOME RARER METALS.

Considerable attention has been given in recent years to the so-called "rare elements," and results of great interest have been obtained in what is undoubtedly a very profitable field of chemical investigation. Nowadays, the description "rare" is not very fitting, for most of them can be obtained in a pure form without difficulty. Apparently, the rare earths of the yttrium group, especially those with odd atomic numbers, are still difficult to obtain pure. Workers on rhenium have been particularly active, but much research remains to be done before the chemistry of this element is satisfactorily elucidated.

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[45] *Ber.*, 1910, **43**, 1200; *A.*, 1910, i, 354.

[46] *J.*, 1934, 56; *A.*, 284.

[47] *Ann. Reports*, 1933, **30**, 108.

[48] F. W. Pinkard, E. Sharratt, W. Wardlaw, and E. G. Cox, *J.*, 1934, 1012; *A.*, 994.

[49] *Compt. rend. Acad. Sci. U.R.S.S.*, 1933, **1**, 218; *A.*, 1934, 379.

Although the account given in the following pages can in no sense claim to be complete, it is hoped that it will provide an indication of the kind of investigation that has been going on in the cases of germanium, gallium, indium, and rhenium.

Germanium.—Discovered in 1886, germanium was considered to be one of the rarest of elements until it was shown in 1916[1] that the spelter residues from certain American zinc ores may contain up to 0·25% of germanium dioxide. Four years later, there was found at Tsumeb, S. W. Africa, a sulphide ore, germanite, stated to have a germanium content of 5—6%, which has been made available in large quantities by the Otavi Minen und Eisenbahn Gesellschaft.[2] There is no doubt that the discovery of these new sources of the element and the improved methods that have been elaborated for its extraction have given an impetus to investigations of this interesting member of the fourth group. From the many contributions which have appeared in recent years, important relationships to carbon and silicon, on the one hand, and tin and lead, on the other, have been established.

In an electrochemical investigation, J. I. Hall and A. E. Koenig[3] have obtained coherent grey deposits of germanium, on copper, by electrolysis of a solution of the dioxide in $3N$-potassium hydroxide at 78—90°, with a low current density. They find that germanium will displace silver from aqueous silver nitrate. An interesting observation has been made with the dioxide, GeO_2.[4] Two crystalline modifications have been identified, one isomorphous with quartz and the other with cassiterite (SnO_2) and plattnerite (PbO_2); a remarkable feature of these two forms is the difference in density (4·28 and 6·26).[5] The literature relating to the hydrides and their halogen derivatives is very voluminous. C. A. Kraus and E. S. Carney[6] have shown that, by treating magnesium germanide with ammonium bromide in liquid ammonia, a yield of 60—70% of mixed germanes can be obtained instead of the possible 22% when hydrochloric acid is employed. Incidentally, it may be mentioned that a mixture of silicon hydrides in good yield is obtained by dropping Mg_2Si into a solution of ammonium bromide in liquid ammonia.[7]

[1] G. H. Buchanan, *J. Ind. Eng. Chem.*, 1916, **8**, 585; *A.*, 1916, ii, 486.

[2] See W. I. Patnode and R. W. Work, *Ind. Eng. Chem.*, 1931, **23**, 204; *B.*, 1931, 495, for references to history of germanite and earlier methods of extraction.

[3] *Trans. Amer. Electrochem. Soc.*, 1934, **65**, 79; *A.*, 735.

[4] V. M. Goldschmidt, *Z. physikal. Chem.*, 1932, **17**, 172; *A.*, 1932, 681; A. W. Laubengayer and D. S. Morton, *J. Amer. Chem. Soc.*, 1932, **54**, 2303; *A.*, 1932, 905.

[5] A. W. Laubengayer and D. S. Morton, *loc. cit.*

[6] *Ibid.*, 1934, **56**, 765; *A.*, 615.

[7] W. C. Johnson and T. R. Hogness, *ibid.*, p. 1252; *A.*, 742.

Particular reference, however, should be made to the isolation of the hydrides $(GeH)_x$ and $(GeH_2)_x$. The monohydride [8] is prepared by the action of cold water on sodium germanide, NaGe, as a dark brown powder which yields germanium and hydrogen at 165°. The dihydride [9] results when calcium germanide, CaGe, is treated with acid. It is an amorphous yellow compound, quite stable when dry but explosively reactive with oxygen. Pyrolysis at 120—220° gives a mixture of GeH_4, Ge_2H_6, Ge_3H_8, and hydrogen with a residue of germanium. The chemical behaviour of $(GeH_2)_x$ indicates an open-chain structure of high molecular weight, analogous to that of the polyoxymethylenes.

A systematic study of certain derivatives of bivalent germanium has given much useful information. The sequence Ge, Sn, Pb indicates that the dichloride should be unstable, and so it is not surprising that it was not isolated until 1929, when L. M. Dennis and H. L. Hunter [10] prepared it as a crystalline, colourless mass by leading the tetrachloride (b. p. 86°) over heated germanium and quickly cooling the vapour. Previously, in most text-books this compound was described as a liquid. Germanium sulphide, GeS, was first described by C. A. Winkler, and a study of its preparation by reduction of the disulphide GeS_2 with hydrogen was made by L. M. Dennis and S. M. Joseph; [11] by this method it is obtained as a black crystalline solid. A red form is obtained when hydrogen sulphide is passed into a hot solution of the dichloride, and the red precipitate dried in nitrogen at 300°. When heated for a few hours in nitrogen at 450°, the red reverts to the black form.[12] It is interesting to notice that the monoxide, GeO, is a jet-black crystalline compound which sublimes in nitrogen at 710°.[12]

Amongst the nitrogen compounds, two nitrides are known, Ge_3N_4 and Ge_3N_2. Germanic nitride [13] can be prepared by the action of gaseous ammonia on germanium at high temperatures or by thermal decomposition of germanic imide, $Ge(NH_2)_2$, which is a light white powder obtained by the ammonolysis of $GeCl_4$ in liquid ammonia. At 150° the imide loses ammonia and forms germanam, Ge_2N_3H, for which the formula (I) has been proposed.[14]

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[8] L. M. Dennis and N. A. Skow, *J. Amer. Chem. Soc.*, 1930, **52**, 2369; *A.*, 1930, 1007.

[9] P. Royen and R. Schwarz, *Z. anorg. Chem.*, 1933, **211**, 412; *A.*, 1933, 579; *ibid.*, 1933, **215**, 295; *A.*, 1934, 158.

[10] *J. Amer. Chem. Soc.*, 1929, **51**, 1151; *A.*, 1929, 662.

[11] *J. Physical Chem.*, 1927, **31**, 1716; *A.*, 1928, 33.

[12] L. M. Dennis and R. E. Hulse, *J. Amer. Chem. Soc.*, 1930, **52**, 3553; *A.*, 1930, 1387.

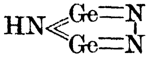
[13] W. C. Johnson, *ibid.*, p. 516; R. Schwarz and P. W. Schenk, *Ber.*, 1930, **63**, [*B*], 296; *A.*, 1930, 437.

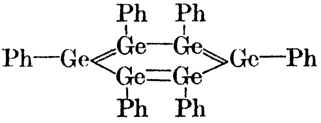
[14] J. S. Thomas and W. Pugh, *J.*, 1931, 60; *A.*, 1931, 322.

Germanous imide[15] may be prepared from the di-iodide and ammonia: $GeI_2 + 3NH_3 = GeNH + 2NH_4I$. When heated to 250—300° for several hours, it gives Ge_3N_2,[16] a finely divided brown powder: $3GeNH = Ge_3N_2 + NH_3$.

Germanium is now included in the list of elements which form heteropolyacids[17, 18] of the type $H_8[X(R_2O_7)_6]$, where R = Mo or W, and X may be one of the following Group IV elements: Si, Ti, Zr, Th, Sn, Pb, Ge, and possibly Hf. The free acid, $H_8[Ge(Mo_2O_7)_6]$,aq., has a varying water content and crystallises in yellow transparent octahedra readily efflorescing, and with m. p. *ca.* 65°.[18] The organo-metallic compounds of germanium have been widely investigated. Amongst the many interesting results obtained, mention may be made of the fact that R. Schwarz and M. Lewisohn[19] have prepared an optically active phenylethyl*iso*propylgermanium bromide, and have also described the aromatic germanium compound (II).

(I.)





(II.)

Finally, there is evidence of the existence of derivatives of pergermanic acid. The per-compounds of the Group IV*a* elements, titanium, zirconium, and thorium, with the general formula H_4MO_5 where M = Ti, Zr, or Th, are well known. In Group IV*b* the tendency to per-acid formation is appreciably less, so that with lead such substances are unknown, and with tin, the perstannate $Na_2Sn_2O_7,3H_2O$ is very unstable.[20] Germanium, however, forms well-defined per-compounds, and Schwarz and Giese have announced the preparation of $K_2Ge_2O_7,4H_2O$, $Na_2Ge_2O_7,4H_2O$, and $Na_2GeO_5,4H_2O$. These authors were unable to isolate a crystalline persilicate, but obtained an oil which may have contained some decomposed persilicate. On the other hand, F. Krauss,[21] by evaporating a solution of sodium silicate treated with hydrogen peroxide, obtained a powder which he considers to be $Na_2SiO_3,H_2O,2H_2O_2$. Evidently he does not regard this product as a true persilicate.

Gallium and Indium.—As gallium is present in nearly all germanium-containing blendes and also occurs in germanite to the extent of *ca.* 0·6%, its extraction generally accompanies that of germanium. The University of Colorado has recently published a "Bibliography of Indium,"[22] in which communications from the date of the discovery of the metal in 1863 to 1933 are classified. Most of the work on indium appears to have been published in Germany and the United States, but the United Kingdom is represented by the work of (Sir) H. C. H. Carpenter and S. Tamura[23] on twinned metallic crystals, some older work of Roberts-Austen and T. Carnelley, and an investigation of indium acetylacetone by H. D. K. Drew and G. T. Morgan.[24]

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[15] W. C. Johnson, G. H. Morey, and A. E. Kott, *J. Amer. Chem. Soc.*, 1932, **54**, 4278; *A.*, 1933, 38.

[16] W. C. Johnson and G. H. Ridgely, *ibid.*, 1934, **56**, 2395.

[17] A. Brukl, *Monatsh.*, 1930, **56**, 179; *A.*, 1930, 1538; R. Schwarz and H. Giese, *Ber.*, 1930, **63**, 2428; *A.*, 1930, 1537.

[18] C. G. Grosscup, *J. Amer. Chem. Soc.*, 1930, **52**, 5154; *A.*, 1931, 322.

[19] *Ber.*, 1931, **64**, 2352; *A.*, 1931, 1435.

[20] R. Schwarz and H. Giese, *Ber.*, 1930, **63**, 780; *A.*, 1930, 720.

[21] *Z. anorg. Chem.*, 1932, **204**, 318; *A.*, 1932, 350.

Within the last few years, important additions to the fundamental chemistry of gallium have been made. Its tri-bromide and tri-iodide were prepared for the first time in 1930,[25] and in the same year it was proved that, not only did sulphides of bi- and ter-valent gallium exist, but also the sulphide of the univalent element.[26] The yellow crystals of Ga_2S_3 were obtained by passing nitrogen and sulphur vapour over the metal at 1200°; when reduced by hydrogen at 800°, it gave a glistening yellow sublimate of GaS, which on being heated in a high vacuum yielded Ga_2S_3 and the volatile Ga_2S. This new sulphide is greyish-black and readily oxidised. A number of selenides have been synthesised:[27] Ga_2Se, GaSe, Ga_2Se_3, In_2Se, InSe, and In_2Se_3, and by the thermal analysis of the systems Ga–Te and In–Te, the existence of the following tellurides has been demonstrated: GaTe, Ga_2Te_3, InTe, and In_2Te_3. The oxide of univalent gallium, Ga_2O, has been obtained[28] but GaO is unknown. A remarkably stable nitride was isolated in 1932 by the interaction of ammonia and gallium at 900°.[29] It is unattacked by concentrated hydrochloric, hydrofluoric, or nitric acid or by hot aqua regia. Even hot concentrated sodium hydroxide dissolves it but slowly. C. A. Kraus and F. E. Toonder[30] have prepared organometallic compounds of gallium which show the expected analogy to the corresponding zinc derivatives. In the third group of the Periodic Table from boron to thallium, either the normal trimethyl or triethyl compounds or both have now been prepared. The series was completed in 1934 by the isolation of trimethylindium,[31] a colourless crystalline solid which gives a molecular weight in benzene in accordance with the polymeride $[In(CH_3)_3]_4$. In the following table, based on that given by W. Klemm,[32] the types of compound that exist for the different valencies are summarised.

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[22] "Studies," 1934, **21**, No. 3.

[23] *Bull. Inst. Min. Met.*, 1928, No. 282; *A.*, 1928, 503.

[24] *J.*, 1924, 1261; *A.*, 1924, i, 941.

[25] W. C. Johnson and J. B. Parsons, *J. Physical Chem.*, 1930, **34**, 1210; *A.*, 1930, 874.

[26] A. Brukl and G. Ortner, *Naturwiss.*, 1930, **18**, 393; *A.*, 1930, 720; *Monatsh.*, 1930, **56**, 358; *A.*, 1930, 1537; W. C. Johnson and B. Warren, *Naturwiss.*, 1930, **18**, 666; *A.*, 1930, 1138.

[27] W. Klemm and H. U. von Vogel, *Z. anorg. Chem.*, 1934, **219**, 45; *A.*, 1081.

[28] A. Brukl and G. Ortner, *Z. anorg. Chem.*, 1931, **203**, 23; *A.*, 1932, 238.

[29] W. C. Johnson, J. B. Parsons, and M. C. Crew, *J. Physical Chem.*, 1932, **36**, 2588; *A.*, 1932, 1218.

[30] *Proc. Nat. Acad. Sci.*, 1933, **19**, 292; *A.*, 1933, 599; *J. Amer. Chem. Soc.*, 1933, **55**, 3547; *A.*, 1933, 1150.

		Valency.				Valency.	
Gallium.	1.	2.	3.	Indium.	1.	2.	3.
Cl	—	+	+	Cl	+	+	+
Br	—	+	+	Br	+	+	+
I	—	—	+	I	+	+	+
O	(+)	—	+	O	(+)	?	+
S	(+)	+	+	S	+	+	+

(+) = Prepared from the gaseous state by cooling but not stable; decomposed on heating; + = prepared by synthesis and stable; — = not yet prepared and probably non-existent.

The summary shows that for both elements uni-, bi-, and tervalent compounds exist. The tendency to exist in the univalent stage is less for gallium than for indium, whilst with thallium it is greatest. Bivalent compounds do not appear to be very stable. In the tervalent state, the halides are almost all colourless; exceptions are GaI_3 and InI_3, which are yellow. Klemm [32] has pointed out an interesting relation between colour and constitution in the compounds of gallium and indium: those of the bivalent stage show no appreciable colour deepening compared with the tervalent stage, whereas the unsaturated compounds of the univalent stage are quite dark. He concludes that this anomaly is explained by the magnetic properties. The bivalent gallium and indium compounds are diamagnetic. Now as $Ga^{\cdot\cdot}$ and $In^{\cdot\cdot}$ ions contain a free electron, they should show paramagnetism. Evidently these ions combine with spin-equalisation to the diamagnetic $(Ga_2)^{IV}$ and $(In_2)^{IV}$ ions, just as two paramagnetic hydrogen atoms form a diamagnetic molecule.

Rhenium.—From the many conflicting statements in the literature, it seems established that rhenium can form three oxides, Re_2O_7, ReO_3, and ReO_2. The colourless heptoxide [33] is obtained by direct oxidation of rhenium. Its m. p. (in vacuum) is 301·5°, and sublimation begins at 220°. In contrast to manganese heptoxide it is very stable, and this is reflected in its large heat of formation, which is approximately 295 kg.-cals. per g.-mol.[34] Under certain experimental conditions it is possible to obtain from the oxidation of rhenium a white crystalline product which (Frau) I. and W. Noddack[35] assumed was the peroxide ReO_4 or Re_2O_8. Later experiments by H. Hagen and A. Sieverts[36] have indicated that this is not a peroxide, but possibly only another form of Re_2O_7. According to W. Biltz[33] and his collaborators, a red trioxide is obtained by the prolonged action of metallic rhenium on the heptoxide at 200—250°, or better, from ReO_2 and Re_2O_7 at 300°. The crystal structure of this trioxide has been examined by K. Meisel,[37] who finds it to be isomorphous with tungsten trioxide, WO_3. The black dioxide ReO_2[38] is formed when Re_2O_7 and Re are heated, first at 300° and then at 600—650°. This dioxide decomposes at 1000° in accordance with the equation : $7ReO_2 = 3Re + 2Re_2O_7$. Certain investigators[39] have claimed that the red oxide is a pentoxide, Re_2O_5, but in view of the results obtained by K. Meisel[37] this appears unlikely. A hydrated Re_2O_3[40] has been prepared by the hydrolysis of rhenium trichloride with aqueous sodium hydroxide. It is readily oxidised and will liberate hydrogen from water. A blue oxide, obtained from the reduction of Re_2O_7, has been mentioned. It may be the analogue of the well-known molybdenum-blue.

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[31] L. M. Dennis, R. W. Work, and E. G. Rochow, *J. Amer. Chem. Soc.*, 1934, **56**, 1047.

[32] *Angew. Chem.*, 1934, **47**, 17.

[33] W. Biltz and G. A. Lehrer (with K. Meisel), *Nach. Ges. Wiss. Göttingen*, 1931, 191; *Chem. Zentr.*, 1932, i, 1070; *A.*, 1932, 708; *Z. anorg. Chem.*, 1933, **214**, 225; *A.*, 1933, 1259; *ibid.*, 1932, **207**, 113; *A.*, 1932, 1008.

In last year's report attention was directed to the isolation of certain halides of rhenium. O. Ruff and W. Kwasnik[41] have continued their investigations on the rhenium fluorides, and have isolated pure ReF_6 (m. p. 18·5°; b. p. 47·6°). This is readily reduced to ReF_4 (m. p. 124·5°) at comparatively low temperatures by a variety of reagents, *e.g.*, hydrogen at 200°, carbon monoxide at 300°, sulphur dioxide at 400°. They have also established the existence of $ReOF_4$ (m. p. 39·7°), ReO_2F_2 (m. p. 156°), and the complex fluoride K_2ReF_6. By contrast, the literature dealing with the action of chlorine on rhenium is very confusing. This confusion began in 1928 with W. Noddack's statement[42] that two volatile chlorides $ReCl_7$ and $ReCl_6$ are formed when rhenium is heated in chlorine. In 1931 H. V. A. Briscoe, P. L. Robinson, and F. M. Stoddart[43] were unable to confirm this, and from their experiments they concluded that the primary product of heating the metal in chlorine was the tetrachloride $ReCl_4$. More recently, however, W. Geilmann, F. W. Wrigge, and W. Biltz[44] report that no tetrachloride can be isolated from this reaction, but that the pentachloride is produced and can be purified by fractional sublimation in a vacuum. These investigators have also prepared a red trichloride from the dark brownish-black pentachloride by heating it in a current of nitrogen. The analytical data[45] for this trichloride show that it is oxygen-free and disprove the suggestion of W. Manchot and J. Düsing[46] that it might be Re_2Cl_6O. J. G. F. Druce[47] claims to have prepared trimethylrhenium from the trichloride. Although a hexafluoride and a pentachloride of rhenium are now known, the highest bromide so far prepared is the tribromide, which H. Hagen and A. Sieverts[48] have isolated as a greenish-black sublimate by heating rhenium at 500° in bromine vapour. It is noteworthy that when the different compounds so far isolated are arranged in the order of their highest valencies, the series becomes Re_2O_7, ReF_6, $ReCl_5$, $ReBr_3$. This is quite in accordance with the general rule that, for a given element, in the series oxides, fluorides, chlorides, bromides, etc., the tendency to reach the highest possible valency decreases.

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[34] W. A. Roth and G. Becker, *Z. physikal. Chem.*, 1932, [*A*], **159**, 1; *A.*, 1932, 469.

[35] *Naturwiss.*, 1929, **17**, 93; *A.*, 1929, 411.

[36] *Z. anorg. Chem.*, 1932, **208**, 367; *A.*, 1933, 43.

[37] *Ibid.*, **207**, 121; *A.*, 1932, 903.

[38] W. Biltz, *ibid.*, 1933, **214**, 225; *A.*, 1933, 1259.

[39] H. V. A. Briscoe, P. L. Robinson, and A. J. Rudge, *J.*, 1931, 3087; *A.*, 1932, 32; W. A. Roth and G. Becker, *Ber.*, 1932, **65**, [*B*], 373; *A.*, 1932, 353.

[40] W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.*, 1933, **214**, 239; *A.*, 1933, 1259.

[41] *Ibid.*, 1934, **219**, 65.

[42] *Z. Elektrochem.*, 1928, **34**, 627; *A.*, 1928, 1344.

The salts of per-rhenic acid offer some marked contrasts to the permanganates. For example, the colourless Re_2O_7 dissolves in water to produce a colourless solution of per-rhenic acid, which forms colourless salts with the alkali and alkaline-earth metals. In addition, an investigation by E. Wilke-Dörfurt and T. Gunzert[49] has revealed striking differences in solubility, crystal form, and content of water of crystallisation between the per-rhenates and the corresponding salts of permanganic, perchloric, and hydrofluoroboric acids. Per-rhenates of the type $M'RO_4$ are generally referred to as meta-salts, for with excess of base it is possible to isolate yellow mesoper-rhenates, $M_3'ReO_5$. The barium salt $Ba_3(ReO_5)_2$, which has been fully described,[50] is decomposed by water into $Ba(OH)_2$

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[43] *J.*, 1931, 2263; *A.*, 1931, 1255.

[44] *Z. anorg. Chem.*, 1933, **214**, 244; *A.*, 1933, 1259.

[45] W. Biltz, W. Geilmann, and F. W. Wrigge, *Annalen*, 1934, **511**, 301; *A.*, 979.

[46] *Ibid.*, **509**, 228; *A.*, 616.

[47] *J.*, 1934, 1129; *A.*, 995.

[48] *Z. anorg. Chem.*, 1933, **215**, 111; *A.*, 1934, 44.

[49] *Ibid.*, p. 369; *A.*, 1934, 158.

[50] (Frau) I. and W. Noddack, *ibid.*, p. 129; *A.*, 1934, 44; B. Scharnow, *ibid.*, p. 185; *A.*, 44.

and $Ba(ReO_4)_2$. A number of similar compounds containing rhenium of lower valency have been reported, but their identity is not yet fully established in every case. A brown rhenite, Na_2ReO_3, is known, and an unstable sand-yellow hyporhenate, possibly $Na_4Re_2O_7$, as well as an unstable green rhenate, $BaReO_4$, have been recorded by (Frau) I. and W. Noddack.[50]

The stable sulphide of rhenium is the black disulphide, ReS_2.[51] A black hydrated sulphide, Re_2S_7, is precipitated when hydrogen sulphide or sodium thiosulphate reacts with potassium per-rhenate, but this is converted into the disulphide when heated in a current of nitrogen.[52]

Some interesting results have been obtained by the electrolytic reduction of acid solutions of rhenium compounds. Reduction of $KReO_4$ in 9*N*-hydrochloric acid, with either a bright or a platinised platinum cathode, gives a green solution containing quinquevalent rhenium.[53] An olive-green solution of tervalent rhenium is obtained by cathodic reduction of K_2ReCl_6 in 2*N*-sulphuric acid.[54] These results are very similar to those obtained with molybdenum compounds, and further work on these electrolytically reduced solutions should yield valuable information about rhenium derivatives.

Finally, it may be mentioned that rhenium forms a number of co-ordination compounds displaying covalencies of four and six, *e.g.*, $PyH[ReBr_4]$, $K_2[ReOCl_5],H_2O$, $X_2[ReCl_6]$, $X_2[ReBr_6]$, where $X = K, Rb, Cs$, etc., and that various oxychlorides and oxybromides are known. The chemistry of rhenium is much more complicated than this short sketch might lead one to suppose, but this statement can be fully confirmed by reference to "Das Rhenium" (Leipzig, 1933) by I. and W. Noddack. W. W.

5. The Corrosion of Metals.

Progress in research on the corrosion of metals has not been reviewed in these Reports during recent years, although occasional reference to results of particular interest has been made. The present Report does not cover any specific period, therefore, but aims at reviewing the trend of research. Space does not permit of the discussion of all the aspects of this work; some of the more fundamental directions of research have been followed at the expense of leaving a certain amount of interesting work unmentioned. A feature of modern views on corrosion is the recognition of the important part played by films, especially those of a protective nature. In order to emphasise this aspect, the results are presented in a somewhat different order from that usually followed.

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[51] I. R. Juza and W. Biltz, *Z. Elektrochem.*, 1931, **37**, 498; *A.*, 1931, 1128.

[52] W. Biltz and F. Weibke, *Z. anorg. Chem.*, 1931, **203**, 3; *A.*, 1932, 238.

[53] W. F. Jakób and B. Jeżowska, *ibid.*, 1933, **214**, 337; *A.*, 1933, 1254.

[54] W. Manchot and J. Düsing, *loc. cit.*, ref. (46).

Film Formation and Passivity.

Progress in the study of passivity, whilst of primary importance from the theoretical viewpoint of corrosion, is one part of the field of corrosion in which considerable unanimity of outlook among investigators all over the world has been reached. Although all are not agreed as to the mechanism, yet it is now generally accepted that passivity is due to the presence of a protective film, generally, but not necessarily, of oxide.

Air-formed Films.—The existence of air-formed oxide films, which interfere with the reactivity of the underlying metal, has been definitely established for copper,[1] aluminium,[2] iron,[3] and certain other metals. Reference has been made in a previous Report[4] to the isolation of the air-formed protective film on iron. These films have since been subjected to further study, particularly with regard to the conditions of their breakdown and their structure. U. R. Evans[5] has shown that breakdown of the protective oxide film on iron, steel, zinc, or aluminium tends to occur where the specimen has been bent or otherwise distorted. Corrosion occurs preferentially at the bend, especially on the convex side.

U. R. Evans and J. Stockdale[6] have put forward a scheme representing the structure of the surface film. This is pictured in four zones: (*a*) an outer zone of oxide, (*b*) a zone containing oxide and metal having a high resistance to attack, (*c*) a shattered zone, fairly free from oxide and having a low resistance to attack, and (*d*) the unchanged metal. They have also devised an improved electrolytic method of isolating the film, by dissolving away (*c*). Flakes of iron oxide, thus isolated from iron heat-tinted to the first-order yellow, were found to have a thickness corresponding with 2×10^{-5} g. of ferric oxide per sq. cm., agreeing with F. H. Constable's[7] determination of the thickness of the film on yellow-tinted iron ($0{\cdot}46 \times 10^{-5}$ cm.).

Passivation in Concentrated Nitric Acid.—Although it has not been possible to isolate an oxide film from iron which has been immersed in concentrated nitric acid, yet this classical example of passivity has been brought into line with the oxide-film theory, for E. S. Hedges [8] obtained convincing evidence of the existence of a film of ferric oxide. Shortly afterwards, C. Benedicks and P. Sederholm [9] examined the effect of dilute alcoholic nitric acid solutions on carbon steels. Owing to the relatively slight dissociation of nitric acid in alcohol, these solutions have something in common as an oxidising agent with concentrated aqueous solutions of nitric acid, and they were shown to render the steel passive and to produce a film of ferric oxide, which was actually photographed. The critical concentration of nitric acid required to render iron and steel passive has been reinvestigated by Y. Yamamoto.[10] Hedges [8] has also shown that other metals are rendered completely passive in concentrated nitric acid at − 11°, and that copper [11] acquires an oxide film in concentrated nitric acid at ordinary temperatures, the existence of which is the cause of the practically complete inertness of this metal when it is kept in motion in this reagent. A. Kutzelnigg [12] has described the passivity of copper in a mixture of nitric and sulphuric acids.

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[1] W. H. J. Vernon, *J.*, 1926, 2273; *A.*, 1926, 1108; F. H. Constable, *Nature*, 1929, **123**, 569; *A.*, 1929, 503.

[2] H. Sutton and J. W. W. Willstrop, *J. Inst. Metals*, 1927, **38**, 259; U. R. Evans, *J.*, 1927, 1039; *A.*, 1927, 619.

[3] *Idem, ibid.*, p. 1021; *A.*, 1927, 619.

[4] *Ann. Reports*, 1928, **25**, 30.

[5] *J.*, 1929, 92; *A.*, 1929, 270.

[6] *Ibid.*, p. 2651; *A.*, 1930, 29.

[7] *Proc. Roy. Soc.*, 1928, [*A*], **117**, 376; *A.*, 1928, 106.

Activating Effects of Ions.—The activating influence of certain anions (especially chlorides) on passive metals has been studied, but it is not yet possible to state definitely whether the effect is due to penetration of the oxide film by anions of small size or whether the activation is related to the well-known peptising effect of chlorides, thus loosening the protective film. The activating effect has been studied [13] by measuring the potential of the metal in the solution against a standard reference electrode. S. C. Britton and U. R. Evans [14] have measured the penetrating powers of different anions by determining the leakage current at an aluminium anode in a solution of potassium chromate, to which solutions containing the ions investigated were added. The following decreasing sequence of penetrating power was noted: chloride>bromide>iodide>fluoride>sulphate>nitrate>phosphate. These results have been confirmed by L. Tronstad and B. W. Bommen.[15] In general, the activating power decreases with increasing size of the anion, but it may be pointed out that a similar rule holds roughly for peptisation. A comparison of the activating effects of various anions on a passive metal with the peptising effect of the same anions on the hydroxide of the metal would be of much interest.

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[8] *J.*, 1928, 969; *Ann. Reports*, 1928, **25**, 30.

[9] *Z. physikal. Chem.*, 1928, **138**, 123; *B.*, 1929, 21.

[10] *Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 375; *A.*, 1934, 736.

[11] E. S. Hedges, *J.*, 1930, 561; *A.*, 1930, 549.

[12] *Z. Elektrochem.*, 1933, **39**, 67; *A.*, 1933, 355.

[13] A. L. McAulay and S. H. Bastow, *J.*, 1929, 85; *A.*, 1929, 270; U. R. Evans, *ibid.*, p. 92; *A.*, 1929, 270; E. S. Hedges, *ibid.*, p. 1037; *A.*, 1929, 775; T. P. Hoar and U. R. Evans, *J. Iron and Steel Inst.*, 1932, **26**, 379; *A.*, 1932, 989.

[14] *J.*, 1930, 1773; *A.*, 1930, 1258.

[15] *K. Norske Vidensk. Selsk.*, 1933, **45**, 174.

The comparative feebleness of the fluoride ion in penetrating or loosening the protective oxide film on iron has been confirmed by A. W. Chapman.[16] In activating passive chromium by cathodic polarisation, E. Müller and K. Schwabe[17] have shown that a definite activation potential is required in different acid solutions, the negative potential increasing in the order: hydrochloric, hydrofluoric, hydrobromic, sulphuric, perchloric, orthophosphoric. The small ions are thus the most powerful. These authors have put forward the view that chromium in the passive state is covered by a network of chromic oxide molecules, anchored to the units of the chromium space lattice. As the cathodic polarisation is increased, the small hydrogen ion is dragged through the oxide network and the electrostatically-bound anion, if it is not too large, can follow it and dissolve the film. Activation is favoured at corners and edges of the metal, because there the oxide network is looser. A short-circuited cell is then set up, and if the potential reaches a higher negative value than the activation potential for the particular acid, the whole metal will become active. With chromium at 20° this is realised only in hydrochloric acid.

Anodic Films.—During the last five years or so a great amount of work on anodic passivity has been carried out by W. J. Müller[18] and his collaborators in Vienna. This important work has not previously been described in these Reports.

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[16] *J.*, 1930, 1546; *A.*, 1930, 1128.

[17] *Z. Elektrochem.*, 1931, **37**, 185; *A.*, 1931, 571; E. Müller, *Z. physikal. Chem.*, 1932, **159**, 68; *A.*, 1932, 473.

[18] W. J. Müller, *Z. Elektrochem.*, 1927, **33**, 401; *A.*, 1928, 135; *Monatsh.*, 1927, **48**, 61; *A.*, 1927, 735; *ibid.*, p. 559; *A.*, 1927, 1145; *Z. Elektrochem.*, 1928, **34**, 571; *A.*, 1928, 1319; *ibid.*, p. 850; *A.*, 1929, 270; *ibid.*, 1929, **35**, 93, 656; *A.*, 1929, 270, 1393; *Monatsh.*, 1929, **52**, 53, 221; *A.*, 1929, 886; *ibid.*, 1930, **56**, 191; *A.*, 1930, 1527; *Z. Elektrochem.*, 1930, **36**, 550; *A.*, 1930, 1257; *ibid.*, p. 679; *A.*, 1930, 1377; *ibid.*, 1931, **37**, 328; *A.*, 1931, 915; *Trans. Faraday Soc.*, 1931, **27**, 737; *A.*, 1932, 25; *Korrosion u. Metallschutz*, 1932, **8**, 253; *A.*, 1933, 576; *Trans. Faraday Soc.*, 1932, **28**, 471; *A.*, 1932, 576; *Z. Elektrochem.*, 1932, **38**, 850; *A.*, 1933, 30; *Angew. Chem.*, 1933, **46**, 197; *A.*, 1933, 468; *Korrosion u. Metallschutz*, 1934, **10**, 1; *A.*, 1178; *Naturwiss.*, 1934, **22**, 479; *A.*, 968; *Z. Elektrochem.*, 1934, **40**, 119, 536, 578; *A.*, 602, 1072; W. J. Müller with E. Noack, *Monatsh.*, 1927, **48**, 293; *A.*, 1927, 942; with K. Konopicky, *ibid.*, p. 711; *A.*, 1928, 247; with O. Löwy, *ibid.*, 1928, **49**, 47; *A.*, 1928, 713; with K. Konopicky, *ibid.*, 1928, **50**, 385; *A.*, 1929, 146; *idem*, *Z. Elektrochem.*, 1928, **34**, 840; *A.*, 1929, 269; *idem*, *ibid.*, p. 858; *A.*, 1929, 146; *idem*, *Z. physikal. Chem.*, 1929, [*A*], **141**, 343; *A.*, 1929, 770; with O. Löwy, *Monatsh.*, 1929, **51**, 73; *A.*, 1929, 402; with K. Konopicky, *ibid.*, 1929, **52**, 289; *A.*, 1929, 1241; with L. Holleck, *ibid.*, 1929, **52**, 409, 425; *A.*, 1930, 298; with K. Konopicky, *ibid.*, p. 442, 463; *A.*, 1930, 298; with W. Machu, *ibid.*,

An essential feature of the experimental conditions is the elimination of disturbances at the anode due to convection. By using a horizontally disposed anode, sheltered from such disturbances, the reaction products remain where they are formed and their properties can be observed. Under these conditions, current density–potential curves for different anodes in various solutions can be made reproducible, and the value determined at which the potential suddenly rises.

One of the most striking results of the work, which appears in the earlier papers, is the complete demonstration that the time during which the current must flow before passivity sets in depends on the current density; passivity can be brought about either by a small current acting for a long time or by a heavy current acting for a short time. This relation suggests that the accumulation of some reaction product at the surface of the anode is responsible for passivity. For a typical case, such as the anodic treatment of iron in dilute sulphuric acid, the view developed is that some product (in this case ferrous sulphate) accumulates at the surface of the anode until the solution in the vicinity becomes supersaturated, whereupon a solid crystallises on the anode surface. The deposit covers a large portion of the surface, increasing the effective current density at the uncovered portions to perhaps 100 or 1000 times the original value. The film is not identified with the protective film causing passivity, but, by screening a large area of the electrode, it may lead to conditions which cause true passivity. Müller calls the first stage "Bedeckungspassivität" and the second stage "chemische Passivität."

To elucidate the relation between the two stages, the rate of fall of current with time has been studied, whilst the composition of the film responsible for "Bedeckungspassivität" has been confirmed in some cases by direct observations with the polarising microscope. In fairly concentrated acids, the films appear to be normal salts, but in more dilute solutions they may consist of basic salts or even oxides or hydroxides.

Assuming that the thickness of the deposited layer remains

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p. 474; *A.*, 1930, 298; *idem*, *Z. physikal. Chem.*, 1931, Bodenstein Festband, p. 687; *A.*, 1931, 1238; *ibid.*, 1932, [*A*], **161**, 147, 411; *A.*, 1932, 993, 1208; with H. K. Cameron and W. Machu, *Monatsh.*, 1932, **59**, 73; *A.*, 1932, 343; with W. Machu, *ibid.*, 1932, **60**, 359; *A.*, 1932, 1000; with E. Löw, *Z. Elektrochem.*, 1933, **39**, 872; *A.*, 1934, 33; with W. Machu, *Z. physikal. Chem.*, 1933, [*A*], **166**, 357; *A.*, 1934, 33; *Monatsh.*, 1933, **63**, 347; *A.*, 1934, 368; with E. Löw, *Z. Elektrochem.*, 1934, **40**, 570; *A.*, 1072.

constant and that the film grows sideways only, the fall of the current i with the time t is given by the expression

$$t = C + A\left[\frac{i}{i_0 - i} + \frac{2\cdot 3}{i_0}\log\frac{i_0 - i}{i - i_R}\right]$$

where i_0 is the initial current, i_R the residual current, and C and A are constants defined by the formulæ

$$C = \frac{s\delta F}{k(1-u)i_0} \text{ and } A = \frac{s\delta^2}{Kk(1-u)w_0}$$

s being the specific gravity of the film material, δ the thickness, F the original area of the anode surface, k the electrochemical constant, u the anionic transport number, w_0 the resistance from the cathode to the boundary layer adjacent to the anode, and K the conductivity of the solution in the boundary layer.

The sideways-growth relation has been confirmed experimentally in sulphuric acid as the electrolyte for anodes of copper, and also for those of iron or nickel in the early stages. In the later stages of anodic passivation, the last two metals follow a course which can be related to the growth of a film in thickness, without sideways extension. Then the currents i_1 and i_2 passing at times t_1 and t_2 are in accordance with the formula

$$t_2 - t_1 = B(1/i_1^2 - 1/i_2^2)$$

where B is a constant depending on the area uncovered. This relation has been confirmed experimentally also for anodes of zinc, chromium, and lead.

In the later papers of the series, Müller definitely accepts the existence of a protective film at passive anodes, but maintains that, when the metal can exist in more than one state of valency, the formation of the film is preceded by an electronic change in the metal. Thus, with an iron anode in dilute sulphuric acid, " Bedeckungspassivität " is due to the primarily-formed film of ferrous sulphate; at unprotected spots, subject to a very high current density, a change is brought about which induces the metal to go into solution as ferric ions; the product is easily hydrolysed, and forms a protective film of ferric oxide on the anode (" chemische Passivität "). With aluminium, where no change of valency occurs, the whole process is regarded as " Bedeckungspassivität." Whether the change of valency observed with some metals is primary or secondary, there is clearly agreement here that anodic passivity, like other forms of passivity, is characterised by the formation of a protective film.

Recent researches have examined quantitatively the degree of protection afforded by the film. Like previous investigators, who have discussed the problem only qualitatively, Müller regards the film as containing pores; the finer the pores, the more protective is the film. He has shown quantitatively how the potential assumed by the metal is related to the number and size of these pores. Qualitatively, the greater the number of pores and the larger their size, the closer the potential approaches that of the underlying metal; on the other hand, when the pores are sufficiently small, corrosion no longer occurs. Thus, the activating influence of chlorides is traced to the relative ease with which such small anions can travel through the pores of the film, whilst larger anions, such as sulphate and phosphate, can penetrate the pores only with difficulty. A film may be efficiently protective, therefore, in solutions containing large anions, but not in solutions containing small anions.

Many of Müller's observations are confirmed by the contemporaneous work of E. S. Hedges [19] on the formation of anodic films on copper, silver, magnesium, zinc, cadmium, mercury, tin, lead, iron, cobalt, nickel, and aluminium. The conditions of study were such that the film automatically appears and disappears periodically, and were thus peculiarly favourable for the study of film formation. In many cases, two definite stages in passivation, corresponding in general with those postulated by Müller, could be observed directly in each recurrent period.

The conditions for periodic anodic film formation or passivity have been elucidated. The experiments show that periodic passivity is simply a special case of periodic film formation, in which the film is highly protective, and that passivity is a general property exhibited to various extents by all metals under suitable conditions, and to different degrees depending on the protective properties of the film under the particular conditions prevailing.

The work has led to a general theory of anodic polarisation, which is confirmed by experiments on the influence of speed of rotation of the anode on periodic anodic passivity, and receives some support from the work of U. R. Evans,[20] who has isolated the film responsible for the passivity of an iron anode in dilute sulphuric acid.

E. Müller and K. Schwabe [21] have studied the formation of films on anodes of zinc, cadmium, lead, and copper in saturated and unsaturated solutions of their salts. Complete passivity is never produced in these systems.

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[19] *J.*, 1926, 1533, 2580, 2678; 1927, 1077, 2710; 1928, 969; 1929, 1028 *A.*, 1926, 807, 1213; 1927 25, 630; 1928, 23, 600; 1929, 775.

[20] *Nature*, 1930, **126**, 130; *A.*, 1930, 1126.

[21] *Z. Elektrochem.*, 1932, **38**, 407; *A.*, 1932, 814.

The formation of films in the dissolution of nickel anodes in acid and salt solutions has been studied by K. Georgi.[22] The potential at low current densities is higher the greater the size of the anion in the series chloride, bromide, sulphate, chlorate. Three states are recognised. The active state is favoured by low current density, small anion, high hydrogen-ion concentration, and high temperature; the reverse conditions favour an impoverished diffusion layer next to the anode and cause transition to a state of higher potential. At the lowest current densities, nickelous ions enter the solution at certain active centres, and hydrogen collects on the greater portion and may be removed by depolarising influences. The second state is characterised by an invisible film of nickelic hydroxide, and the third by a porous diaphragm of the same hydroxide. Georgi obtained similar results with anodes of cobalt and iron.[23]

The passivity of copper anodes in sulphuric acid[24] and of gold anodes in hydrochloric and sulphuric acids[25] has been traced to the formation of oxide or similar films. The mechanism of the anodic passivity of gold in chloride solutions has been further studied by G. Armstrong and J. A. V. Butler.[26] The nature of the anodic oxide film formed on aluminium in oxalic acid has been investigated by S. Setoh and A. Miyata.[27]

Optical and Other Means of Investigation.—The air-formed film has been recognised by optical means by H. Freundlich, G. Patscheke, and H. Zocher,[28] who prepared mirrors of pure iron by the thermal decomposition of iron pentacarbonyl in absence of air. When air was admitted, a fall in the reflecting power of the mirrors was observed, and the chemical reactivity of the iron was reduced simultaneously.

L. Tronstad[29] has applied the optical method to the examination of anodic passivity, and shown that the optical constants of nickel and iron rendered passive in sodium hydroxide solution, and of nickel rendered passive in sulphuric acid solution, undergo a change

[22] *Z. Elektrochem.*, 1932, **38**, 681, 714; *A.*, 1932, 1000, 1093.

[23] *Ibid.*, 1933, **39**, 209, 745; *A.*, 1933, 468, 1016.

[24] M. Lignana, *Nature*, 1932, **130**, 474; *A.*, 1932, 1208.

[25] W. J. Shutt and A. Walton, *Trans. Faraday Soc.*, 1932, **28**, 740; *A.*, 1932, 1209; *ibid.*, 1933, **29**, 1209; *A.*, 1933, 1242; *ibid.*, 1934, **30**, 914; *A.*, 1178.

[26] *Ibid.*, p. 1173.

[27] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1932, **19**, 189, 237; *A.*, 1933, **29**, 1254.

[28] *Z. physikal. Chem.*, 1927, **128**, 321; **130**, 289; *A.*, 1927, 1037, 1149.

[29] *Nature*, 1929, **124**, 373; *A.*, 1929, 1150; *Z. physikal. Chem.*, 1929, **142**, 241; *A.*, 1929, 1002; *K. Norske Vidensk. Selsk.*, 1931, No. 1; *Nature*, 1931, **127**, 127; *A.*, 1931, 301; *Trans. Faraday Soc.*, 1933, **29**, 502; *A.*, 1933, 459.

resembling that observed when a clean iron surface is brought from a vacuum into contact with air. This result points directly to the formation of an oxide film during anodic passivation. L. Tronstad and C. W. Borgmann[30] have shown by the optical method that when iron, steel, or stainless steel is immersed in potassium chromate solution or concentrated nitric acid, the natural, air-formed films are strengthened or even replaced by denser films, in accordance with the oxide theory of passivity. Approximate calculations give 100 Å. for the thickness of the oxide film formed on steel in nitric acid, and 30—40 Å. for that formed in a chromate–chloride solution. The thickness of the film on stainless steel in concentrated nitric acid was only 10 Å. Similar experiments indicate that the natural oxide film on aluminium[31] has a thickness of 100 Å. and undergoes only small changes in chromate solutions. The optical method also shows[32] that in dry ozone highly protective films are obtained on silver, iron, and ordinary and stainless steels, whereas less protective films are acquired by copper and zinc. In moist ozone, no highly protective films are produced.

On the whole, relatively little help has been gained by the application of *X*-ray and electron-diffraction technique to the elucidation of the structure of the film. F. Krüger and E. Nähring[33] obtained identical *X*-ray diagrams for active and passive iron, nickel, and chromium in the finely-divided condition, and considered that any oxide film present could not be thicker than 10^{-7} cm. Actually, there is no reason why a really continuous protective film need exceed 10^{-7} cm. in thickness; moreover, in some cases the film may not have a crystalline space-lattice.

G. P. Thomson[34] has found no difference in the electron-diffraction patterns of active and passive iron; but it should be pointed out that neither aluminium covered with the usual air-formed film, nor lead, freshly cut and heated in the air at about 100°, gave a diffraction pattern in his experiments. J. A. Darbyshire,[35] however, after isolating the oxide films on heat-tinted nickel and copper by Evans's method, has demonstrated their crystalline nature by the electron-diffraction method. The spacings obtained indicate the formulæ NiO and Cu_2O for these oxides. The electron-diffraction pattern of iron rust has been obtained by J. Cates.[36] C. A. Murison[37] has found that surface films on copper heated in air give diffraction patterns for cuprous oxide and a new form of cupric oxide. Diffraction patterns have been obtained from oxide films on zinc by G. I. Finch and A. G. Quarrell.[38]

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[30] *Trans. Faraday Soc.*, 1934, **30**, 349; *A.*, 486.

[31] L. Tronstad and T. Höverstad, *Trans. Faraday Soc.*, 1934, **30**, 362; *A.*, 486.

[32] *Idem, ibid.*, p. 1114.

[33] *Ann. Physik*, 1927, **84**, 939.

[34] *Proc. Roy. Soc.*, 1930, [*A*], **128**, 649; *A.*, 1930, 1082.

[35] *Trans. Faraday Soc.*, 1931, **27**, 675.

[36] *Ibid.*, 1933, **29**, 817; *A.*, 1933, 1022.

[37] *Phil. Mag.*, 1934, [vii], **17**, 96; *A.*, 134.

Corrosion in Aqueous Solutions.

Neutral Media.—A vigorous campaign to determine the mechanism of the corrosion of metals in neutral aqueous solutions has been made during the last few years by Bengough and his collaborators.[39] The work has aimed at acquiring quantitative data for the extent and nature of corrosion under different conditions, and has been concerned especially with the corrosion of zinc and mild steel in neutral salt solutions, such as potassium chloride, over a wide range of concentration. Special attention has been devoted to reproducibility of the results. The influence of various factors, such as concentration, depth of immersion of the specimen, convection, access of oxygen, purity and treatment of the metal, and nature of its surface, has been studied, and it has been possible in many cases to ascertain which is the controlling factor in a given set of circumstances. Two types of corrosion have been recognised, corresponding with evolution of hydrogen and absorption of oxygen.

Concurrently with the kinetic measurements, the course and distribution of corrosion have been followed by microscopical observation. It is held that certain of the results cannot be accounted for by the differential aeration theory. The initial behaviour of zinc, when placed in a salt solution which does not form a passivating film, is to displace hydrogen at numerous points. The possibility of the production of gaseous hydrogen being neglected, a polarising layer is formed at the metal surface. The oxygen present is required for depolarisation; if the anions present form a soluble salt with the metal and are plentiful, corrosion proceeds at a rate which is directly proportional to the oxygen supply.

When zinc corrodes in solutions of potassium sulphate or chloride in presence of oxygen, the film of zinc oxide formed is in parts continuous, impermeable to oxygen, and closely adherent to the metal, and in parts in the form of "domes," which are loose and permeable to oxygen. Corrosion is most serious under the "domes." The authors point out that, if the protective type of hydroxide film is formed over a part of the metal, corrosion can only occur elsewhere; they maintain that the preferential corrosion under the " domes " is not due to potential differences set up by difference of oxygen concentration, but to the fact that ions can freely enter solution there. Other portions of the metal surface are prevented from undergoing local dissolution by the protective film, which, however, allows depolarisation of hydrogen displaced by metal entering the solution elsewhere.

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[38] *Proc. Physical Soc.*, 1934, **46**, 148; *A.*, 352.

[39] G. D. Bengough, J. M. Stuart, and A. R. Lee, *Proc. Roy. Soc.*, 1927, [*A*], **116**, 451; *A.*, 1928, 250; *ibid.*, 1928, [*A*], **121**, 88; *A.*, 1928, 1333; *ibid.*, 1930, [*A*], **127**, 42; *A.*, 1930, 712; G. D. Bengough, A. R. Lee, and F. Wormwell, *ibid.*, 1931, [*A*], **131**, 494; *A.*, 1931, 691; *ibid.*, 1931, [*A*], **134**, 308; *A.*, 1932, 27; G. D. Bengough and F. Wormwell, *ibid.*, 1933, [*A*], **140**, 399; *A.*, 1933, 679.

According to the " film-distribution " theory advanced, dissolved oxygen is not really an inhibitor of corrosion, but a stimulator; it may act as a local inhibitor owing to the formation of secondary products, which prevent access of oxygen to the underlying metal and the entrance of ions into solution, but corrosion is proportionally increased elsewhere. Thus, corrosion distribution is determined mainly by the distribution of protective films, which cause the metal to be locally cathodic to bare, or less completely protected, metal. When the films are widespread, corrosion may be sufficiently localised to be called " pitting." Among the factors influencing the character, distribution, and continued adherence of the films are distribution of alkali, surface tension, presence of specially reactive areas, gravity, movement of liquid, alternate wet and dry conditions, the presence of foreign substances, and the nature of the solution.

Simultaneously, Evans and his collaborators [40] have continued researches the results of which support the differential æration theory, some of the systems investigated being similar to those examined by Bengough and his colleagues. It has been shown that, under conditions favouring the complete tapping of the electric currents flowing between the anodic and cathodic portions of the corroding metal, the currents measured are equivalent to the corrosion occurring, both when the anodes and cathodes are of different metals and when the anodic and cathodic areas of the same metal are determined by differences in oxygen concentration. The problem of corrosion velocity is thus resolved into a study of the electrochemical factors which determine the strength of the current. It is pointed out that the experiments of Bengough and his co-workers have been carried out under conditions which reduce the possibility of differential æration to the minimum.

The objections of the Bengough school to the differential-æration theory are further answered by C. W. Borgmann and U. R. Evans [41] in a paper describing work on the corrosion of zinc in chloride solutions. There, it is shown that different results are obtained accordingly as the specimens are partly or wholly immersed in the solution. The apparent discrepancy between the results obtained with half-immersed sheet zinc and Bengough's results with totally immersed zinc is traced to the avoidance of oxygen starvation in the partly-immersed specimens.

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[40] U. R. Evans, L. C. Bannister, and S. C. Britton, *Proc. Roy. Soc.*, 1931, [*A*], **131**, 355; *A.*, 1931, 691; U. R. Evans and T. P. Hoar, *ibid.*, 1932, [*A*], **137**, 343; *A.*, 1932, 1003.

[41] *Trans. Amer. Electrochem. Soc.*, 1934, **65**, 249.

U. R. Evans and R. B. Mears,[42] replying to further criticisms by Bengough, agree that the film-distribution theory and the differential-æration theory have much in common, which is concealed by the mode of presentation; in particular, the views agree in ascribing protection largely to the cathodically-formed alkali. Differences of opinion exist as to the effect of solid corrosion products on oxygen transport, and the possible inhibition of corrosion by excess of oxygen. Further work in support of both the theories of differential æration and film distribution will be awaited with great interest; to many who are following the work it may appear that the two schools of thought are by no means irreconcilable.

In a study of the effect of non-metallic inclusions on the corrosion of mild steels, C. E. Homer [43] has shown that under mildly corrosive conditions (*e.g.*, in tap water, distilled water, etc.) sulphide and scale inclusions determine the initial points of attack. Only a small proportion of such inclusions has any effect, however, and inclusions of silicates or alumina are inactive. The action appears to be connected closely with the breakdown of the protective oxide film. No evidence was obtained that either sulphide or scale inclusions act as cathodes in the corrosion process. Under conditions favouring pitting, the initial breakdown may determine the sites of pitting. Similar conclusions have been reached by L. Tronstad and J. Sejersted,[44] who have investigated the effect of sulphur and phosphorus on the corrosion of iron.

J. N. Friend and W. West [45] have shown that the addition of copper up to 3·70% increases the resistance of nickel steel to alternate wet and dry sea action. F. Tödt [46] has studied the influence of oxidising and reducing agents on the corrosion of iron in buffered solutions. The corrosion of tin, tin–antimony, and tin–antimony–copper alloys in various tap-waters has been described by T. P. Hoar.[47]

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[42] *Proc. Roy. Soc.*, 1934, [*A*], **146**, 153; *A.*, 1181.

[43] *Iron and Steel Inst.*, Carnegie Schol. Memoirs, 1932, **21**, 35; Special Report No. 5, 1934, 225.

[44] *J. Iron and Steel Inst.*, 1933, **127**, 425.

[45] *Ibid.*, 1931, **123**, 501; *B.*, 1931, 637.

[46] *Z. Elektrochem.*, 1934, **40**, 536; *A.*, 973.

[47] *J. Inst. Metals*, 1934, **55**, 135.

The theory of the corrosion of metals has been discussed [48] and some new views have been put forward. E. S. Hedges [49] has outlined a theory involving primary reaction of the metal with water molecules, the extent of the corrosion depending on the degree to which the initially formed hydroxide film is dissolved or peptised by the solution, and almost simultaneously A. L. McAulay and E. C. R. Spooner [50] have advanced the view that electrode potential must originate in interaction between the metal and water only. U. R. Evans and T. P. Hoar [51] have discussed the mechanism of corrosion in the light of both cathodic and anodic processes, and have emphasised the important rôle of the relative solubility of the reaction products.

The Dissolution of Metals in Acids.—In the course of work on the dissolution of sodium amalgam in weak acid solutions, J. N. Brönsted and N. L. R. Kane [52] discuss the wider aspects and conclude that the dissolution of a pure metal in an acid is probably the result of a chemical reaction between an electron of the metal and a molecule of the acid.

G. Tammann and F. Neubert [53] have found that the rate of evolution of hydrogen from dilute acids when acted on by zinc, iron, or aluminium can be expressed by $v = a\,t + b\,t^2$, where v is the volume liberated at the time t. The constant a is characteristic of the metal and is unaffected by impurities, whilst the constant b represents the accelerating influence of heterophase impurities forming local electrolytic cells.

The velocity of the dissolution of zinc in acids has been the subject of several papers. E. Müller and J. Förster [54] have studied particularly the influence of the concentration of the acid and the nature of the anion. M. Centnerszwer and M. Straumanis [55] have shown that electrolytic zinc dissolves much more slowly in dilute sulphuric acid than in hydrochloric acid of the same hydrogen-ion concentration. The velocity of dissolution is related to the concentration (C) of hydrochloric acid (up to $2N$) by the linear equation $dv/dt = k(C - C_0)$, where C_0 is the threshold concentration of acid at which dissolution begins, and k is a constant. The value of the temperature coefficient and the influence of stirring confirm that the velocity of this reaction is controlled by the chemical process, not by the diffusion of the acid. The dissolution is preceded by an induction period, which can be eliminated by previously rubbing the zinc with emery paper.[56] The influence of various addenda, especially hydrophilic colloids, on the rate of dissolution of zinc and iron in hydrochloric acid has been investigated by M. Schunkert.[57] O. Bauer and P. Zunker [58] have studied the influence of small quantities of alloying elements on the rate of dissolution of zinc in hydrochloric acid, and shown that the results are not necessarily parallel with those obtained in neutral salt solutions.

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[48] M. Straumanis, *Korrosion u. Metallschutz*, 1933, **9**, 1, 29; O. P. Watts, *Trans. Amer. Electrochem. Soc.*, 1933, **64**, 219; *A.*, 1933, 1122.

[49] "Protective Films on Metals," London, 1932, p. 165.

[50] *Proc. Roy. Soc.*, 1932, [*A*], **138**, 494; *A.*, 1933, 28.

[51] *Trans. Faraday Soc.*, 1934, **30**, 424; *A.*, 606.

[52] *J. Amer. Chem. Soc.*, 1931, **53**, 3624; *A.*, 1931, 1373.

[53] *Z. anorg. Chem.*, 1931, **201**, 225; *A.*, 1932, 128.

[54] *Z. Elektrochem.*, 1932, **38**, 901; *A.*, 1933, 130.

[55] *Z. physikal. Chem.*, 1934, [*A*], **167**, 421; *A.*, 370.

L. Whitby [59] has found that, whilst the rate of dissolution of 99·90% magnesium in 0·05*N*-hydrochloric acid is independent of the impurities in the metal, large variations are observed for different samples in sodium chloride; these are traced to the effect of films formed at the cathodic parts of the surface, whilst in the acid solutions film formation is prevented. The rate of dissolution of magnesium in dilute acids has also been studied by M. Kilpatrick and J. H. Rushton,[60] who direct attention to the part played by water. R. Müller [61] concludes, from measurements of the velocity coefficient of the dissolution of aluminium with hydrochloric acid, that the reaction occurs with HCl–H_2O complexes.

The Corrosion of Tinplate.—The use of tinplate as a food container has encouraged considerable activity during recent years in the investigation of the conditions of corrosion of tin, iron, tinplate, and the tin–iron couple in various aqueous solutions, notably those of weak acids. The existence of discontinuities in the tin coating of tinplate might be expected to lead to serious local corrosion at the exposed steel. Experiments [62] have shown, however, that under certain conditions the potential of the tin–iron couple is reversed, tin becoming anodic to iron. Under these conditions the attack is not localised at small areas, and the tinplate gives more useful service. Different explanations of this phenomenon have been advanced, the reversal of potential being ascribed to film formation on one or both of the metals, or to the high hydrogen overpotential of tin. T. P. Hoar [63] states that tin is anodic to iron in citric and oxalic acid solutions, owing to the removal of tin ions as complexes, whilst in dilute sulphuric acid, where such complexes are not formed, tin remains cathodic to iron.

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[56] *Z. physikal. Chem.*, 1934, [*A*], **167**, 421; *A.*, 370.

[57] *Ibid.*, 1933, [*A*], **157**, 19.

[58] *Z. Metallk.*, 1933, **25**, 282.

[59] *Trans. Faraday Soc.*, 1933, **29**, 415, 853; *A.*, 1933, 233, 1017.

[60] *J. Physical Chem.*, 1934, **38**, 269; *A.*, 605.

[61] *Z. Elektrochem.*, 1934, **40**, 126; *A.*, 605.

[62] C. L. Mantell and W. G. King, *Trans. Amer. Electrochem. Soc.*, 1927, **51**, 40; *B.*, 1927, 632; R. H. Lueck and H. T. Blair, *ibid.*, 1928, **54**, 257; *B.*, 1928, 819; E. F. Kohman and N. H. Sanborn, *Ind. Eng. Chem.*, 1928, **20**, 76, 1373; *B.*, 1928, 159.

[63] *Trans. Faraday Soc.*, 1934, **30**, 472; *A.*, 735.

An improved method of detecting discontinuities in the tin coating of tinplate, by observing the sites of rust formation when the carefully cleaned specimen is immersed for some hours in hot distilled water within a certain p_H range, has been described by D. J. Macnaughtan, S. G. Clarke, and J. C. Prytherch.[64]

T. N. Morris and J. M. Bryan [65] have undertaken a systematic investigation of the corrosion of tinplate, studying in particular the effect of a typical fruit acid (*e.g.*, citric acid) in dilute solution on (*a*) the steel base of tinplate, (*b*) tin, (*c*) the tin–iron couple, (*d*) tinplate. The investigation has also included a study of the influence of p_H, presence of oxygen, and the corrosion products on the further corrosion of these materials; *e.g.*, the influence of tin salts on the corrosion of iron, and of iron salts on the corrosion of tin and iron in the presence and in the absence of air.

The corrosion of tinplate in various dilute acids has been investigated by G. Gire,[66] who has also emphasised the important rôle of the presence of oxygen.

Atmospheric Corrosion.

In the field of atmospheric corrosion the need of well-planned, comprehensive researches, extending over a period of many years, has been realised, and work is in progress in many parts of the world. Up to the present, insufficient time has elapsed to enable the final results to be anticipated. The earlier work of W. H. J. Vernon for the Atmospheric Corrosion Research Committee of the British Non-Ferrous Metals Research Association has already been reported upon.[67]

A Joint Corrosion Committee of the Iron and Steel Institute and the National Federation of Iron and Steel Manufacturers began in 1928 a comprehensive series of field tests under well-defined conditions and over prolonged periods. A special feature of the work is that all the materials tested are of known origin and have usually been manufactured in the presence of members of the Committee; full particulars have been recorded regarding their manufacture, casting, and rolling, and each specimen can be traced back to its exact position in the ingot. The investigations cover the effects of (1) surface condition, (2) the presence of rolling scale and of variations in the type of scale, (3) the nature of the basis metal and method of preparation of the surface on the protection afforded by coatings of paint, (4) copper content on the corrosion of mild steel, and also (5) comparisons of ingot iron and several types of wrought iron and (6) tests on high-tensile steels.

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[64] *J. Iron and Steel Inst.*, 1932, **25**, 159; *B.*, 1932, 605.

[65] D.S.I.R., Food Investigation Bd. Special Report, No. 40, 1931; *B.*, 1931, 591; Report of the Director of Food Investigation, Section E, 1932 and 1933; *Trans. Faraday Soc.*, 1933, **29**, 395, 830; 1934, **30**, 1059.

[66] *Rev. Trav. Office Pêches Maritimes*, 1930, **3**, 409; 1931, **4**, 355; 1933, **6**, 305.

[67] *Ann. Reports*, 1928, **25**, 29.

The tests are being carried out under widely different climatic conditions at four main stations in Great Britain and ten subsidiary stations in Great Britain and abroad. Marine, moorland, highly industrial, and urban atmospheres are comprised, as well as tests in railway tunnels, etc., and under arctic and tropical conditions. Comparative tests under service conditions are being conducted in different types of atmosphere on railway sleepers of the same steel with and without addition of copper. The specimens have been weighed and will be removed periodically in batches in order to enable corrosion–time curves to be constructed.

A Sub-Committee on Laboratory Corrosion Tests has also been formed to develop laboratory tests to give a true index of service behaviour. An improved, automatic, spray test has been recommended. Further work has been done on corrosion testing by examining the alteration of mechanical properties.

When the final results of this comprehensive research programme are available, it may confidently be expected that the knowledge of certain aspects of atmospheric corrosion will be considerably advanced. In the meantime two reports have been published.[68]

Simultaneously, the Committees on Corrosion of Iron and Steel and on Corrosion of Non-Ferrous Metals and Alloys of the American Society for Testing Materials have continued and extended their work on atmospheric corrosion, which has been in progress for many years. Some of the more recent results have been set forth and discussed in a Symposium on the Outdoor Weathering of Metals and Metallic Coatings.[69] This discussion is of a practical nature and is intended to illustrate certain proper uses to which the test data may be put by engineers.

Continuing his work for the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research, W. H. J. Vernon [70] has studied the corrosion of copper in certain synthetic atmospheres in the laboratory, with special reference to the influence of sulphur dioxide in air at different relative humidities. He has described an air thermostat, suitable for use in work of this kind,[71] and a method has been worked out [72] for the preparation of atmospheres of any desired relative humidity. The rôle of the moisture in iron rust in determining the critical corrosion humidity is explained in colloid-chemical terms by W. S. Patterson and L. Hebbs.[73] P. R. Kosting [74] has conducted accelerated weathering tests on soldered and tinned-sheet copper in atmospheres rich in sulphur dioxide and carbon dioxide.

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[68] *Iron and Steel Inst.*, Special Report No. 1, 1931; Special Report No. 5, 1934; discussion, *J. Iron and Steel Inst.*, 1934, **129**, 357.

[69] *Amer. Soc. Testing Materials*, 1934, Pre-print.

[70] *Trans. Faraday Soc.*, 1931, **27**, 255; *B.*, 1931, 763.

A study by W. H. J. Vernon and L. Whitby [75] of the green patina which forms on the surface of copper exposed to different types of atmosphere, has shown that, contrary to the former belief, the patina consists mainly of basic copper sulphate. In the course of time its composition accords with that of the mineral brochantite, $CuSO_4,3Cu(OH)_2$. In seaside districts the patina may contain copper chloride, but the basic sulphate predominates when urban and marine conditions coincide. The sulphate is obtained from sulphurous and sulphuric acids brought into the atmosphere through the combustion of coal. There seems to be no doubt that the longevity of copper exposed to the atmosphere is due to the protective properties of the film of basic sulphate. Methods have been worked out,[76] therefore, for the rapid production of an artificial patina of this substance by anodic treatment of the copper in a suitable electrolyte. Other artificial methods have been described by J. R. Freeman and P. H. Kirby.[77]

L. Whitby [78] has shown that magnesium carbonate predominates in the corrosion product of magnesium in indoor or outdoor atmospheres. No indication of the formation of a protective film was observed. The rate of corrosion increases with the relative humidity of the atmosphere.

A reflectivity method for measuring the tarnishing of highly-polished metals has been described by L. Kenworthy and J. M. Waldram,[79] and some results obtained by this method for tin and Britannia metal are given. E. S. H.

E. S. HEDGES.
W. WARDLAW.
R. WHYTLAW-GRAY.

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[71] *Trans. Faraday Soc.*, 1931, **27**, 241; *A.*, 1931, 815.

[72] W. H. J. Vernon and L. Whitby, *ibid.*, p. 1; *A.*, 1931, 816.

[73] *Ibid.*, p. 278; *B.*, 1931, 762.

[74] *Bur. Stand. J. Res.*, 1932, **8**, 365; *B.*, 1932, 553.

[75] *J. Inst. Metals*, 1929, **42**, 181; *B.*, 1929, 855; *ibid.*, 1930, **44**, 389; *B.*, 1930, 992; W. H. J. Vernon, *ibid.*, 1933, **52**, 93; *B.*, 1933, 633; *J.*, 1934, 1853.

[76] *Idem*, *J. Inst. Metals*, 1932, **49**, 153; *B.*, 1932, 940.

[77] *Metals and Alloys*, 1932, **3**, 190; *B.*, 1932, 986; *ibid.*, 1934, **5**, 67.

[78] *Trans. Faraday Soc.*, 1933, **29**, 844; *A.*, 1933, 1017.

[79] *J. Inst. Metals*, 1934, **55**, 247.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

Stereochemistry.

THE numbers of theoretically possible structural isomerides in series of aliphatic compounds, though seldom required for stereochemical purposes, are of some interest as giving perspective. The following are from the calculations of H. R. Henze and C. M. Blair [1] for saturated aliphatic open-chain series :

No. of C atoms.	Hydrocarbons.	Alcohols.	Esters.	Disubstituted paraffins, $C_nH_{2n}X_2$.	$C_nH_{2n}XY$.
5	3	8	9	21	31
10	75	507	599	2,261	3,959
15	4,347	48,865	57,564	312,246	576,221
20	366,319	5,622,109	6,589,734	46,972,357	88,594,746

Efforts to calculate the valency angles of carbon, oxygen, and sulphur in various open-chain and cyclic compounds have been continued by a number of workers, who have usually proceeded from determinations of dipole moment or from *X*-ray diagrams. The valency angle for oxygen in ethylene oxide is [2] 115° ± 7° ; in diphenyl ether,[3] 142° ± 8° ; in phenols, 137° ; in anisoles, 150° ; in diphenylene dioxide,[4] 120° ; in water,[3] 134° ; in dimethyl ether, 115° ± 7° [2] or 147°.[3] That for sulphur, in diphenyl sulphide,[3] is 118° ± 8° ; in thianthren,[2] which is non-planar, is $< 120°$; in potassium trithionate [5] the third S atom forms two linkings both with sulphur atoms, at 103°. On the other hand, J. S. Allen and H. Hibbert give some values [6] for the oxygen valency angle in the simpler rings which are considerably lower than the tetrahedral angle, as might be anticipated from the strain theory : in ethylene oxide and in propylene oxide, 70° ; in trimethylene oxide, 94° ; in tetrahydrofuran, 108° ; in tetrahydropyran (pentamethylene oxide), 93°. They regard the tetrahydropyran ring as puckered (diplanar) and strainless, whereas the tetrahydrofuran ring is planar and strained, thus accounting for the fact that in the carbohydrates the pyranose ring is more stable than the furanose; the greater stability of the γ- over the δ-lactones, however, presents an obstacle. The valency angle of carbon in diphenylmethane[3] is 115° ± 5°, which may be close to the tetrahedral angle (109° 28′). W. G. Penney calculates[7] that in ethylene the carbon valency angles (to the pairs of H atoms) are about 130°. Many of the estimates of valency angles quoted above differ considerably from previous estimates, so it may be concluded that the available methods are as yet not sufficiently advanced to solve the problems of the angles present in chains and heterocyclic rings.

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[1] *J. Amer. Chem. Soc.*, 1934, **56**, 157; *A.*, 276. See also *idem*, *ibid.*, 1931, **53**, 3042, 3077; 1933, **55**, 680; L. Coffman and C. M. Blair with H. R. Henze, *ibid.*, 1933, **55**, 252.

[2] G. M. Bennett, *Trans. Faraday Soc.*, 1934, **30**, 853; *A.*, 1157.

[3] G. C. Hampson, R. H. Farmer, and L. E. Sutton, *Proc. Roy. Soc.*, 1933, [*A*], **143**, 147; *A.*, 1934, 131.

[4] G. M. Bennett, D. P. Earp, and S. Glasstone, *J.*, 1934, 1179; *A.*, 1058.

[5] W. H. Zachariasen, *J. Chem. Physics*, 1934, **2**, 109; *A.*, 479.

[6] *J. Amer. Chem. Soc.*, 1934, **56**, 1398; *A.*, 831.

Several interesting deductions from *X*-ray work on the shape of organic molecules have been published. In $CHBr_3$ the angle between the C–Br linkings is 115°, in CH_2Br_2 it is 125° (as is also the angle between the C–I linkings in CH_2I_2); in CMe_3Br the distribution of the four groups about the central carbon atom is tetrahedral.[8] The structures of *cis*- and *trans*-$C_2H_2Br_2$, C_2HBr_3, $CH_2\colon CHBr$, C_2Cl_4, and C_2HCl_3 are all planar,[9] with interatomic distances C–C of 1·3 Å., as against 1·55 Å. for C–C(H_3) in CMe_3Br. Durene[10] consists of a regular plane hexagonal ring, with the four Me groups in the plane of the ring but displaced slightly towards the unsubstituted positions; the distance C–C is 1·41 Å. in the ring and 1·47 Å. from chain to ring. Naphthalene[11] consists of two regular plane hexagons, with C–C 1·41 Å. Chrysene[12] is planar and consists of regular hexagons, with C–C again 1·41 Å. In *o*- and *p*-$C_6H_4Cl_2$ vapours the molecules are planar or nearly so.[13] These results are all in harmony with those based on the classical methods. On the other hand, the molecules of *s*-triphenylbenzene are stated[14] to be asymmetric.

Geometrical Isomerides.—Several studies among simpler polymethylene ring derivatives have been made, which continue earlier knowledge. Of *cis*- (m. p. 115—117°) and *trans*- (m. p. 230—231°) 1 : 2-dimethyl*cyclo*propane-1 : 2-dicarboxylic acid,[15] the former gives a simple anhydride (m. p. 54—56°) with acetyl chloride, and the latter only a polymeric anhydride; the dissociation constants of the acids have been determined. Isomerisation of the *cis*-acid with hydrochloric acid leads to fission of the ring; but *cis-cyclo*-butane-1 : 2-dicarboxylic acid (m. p. 138—139°) gives the *trans*-acid with that reagent at 190°; the dissociation constants of these acids also are given.[16] *trans-cyclo*Heptane-1 : 2-diol has been resolved[17] by crystallisation of the strychnine salt of its hydrogen sulphate from alcohol; the liberated dihydroxy-compound had $[\alpha]_{5460}$ −44·25° in water. Two stereoisomeric forms of αα′-diphenyltetrahydro-γ-pyrone (m. p. 131° and m. p. 76°) have been prepared.[18] Some interesting derivatives of hydrindene have been examined[19] by D. H. Peacock and B. K. Menon; β-phenyl-α-1-hydroxyhydrindene-2-propionic acid was obtained as a *trans*-compound (I), since it did not readily form a lactone; but when it was treated with hydrogen bromide in acetic acid it was presumably isomerised to the *cis*-compound, since a lactone (II) was then formed. If the acid (I) was esterified and the *p*-toluenesulphonyl derivative of this ester treated with ammonia, another lactone (III) was obtained, which could also be prepared by the action of alkali upon (II); inversion of the configuration of the asymmetric carbon of the side chain had therefore been effected. The lactone, like the acid, contains three structurally different asymmetric carbon atoms and would therefore be able to assume four racemic forms if the *trans*- as well as the *cis*-lactone bridge could be produced.

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[7] *Proc. Roy. Soc.*, 1934, [*A*], **144**, 166; *A.*, 476.

[8] R. W. Dornte, *J. Chem. Physics*, 1933, **1**, 630; *A.*, 1934, 18.

[9] *Idem*, *ibid.*, p. 566; *A.*, 18.

[10] J. M. Robertson, *Proc. Roy. Soc.*, 1933, [*A*], **142**, 659; *A.*, 1934, 18.

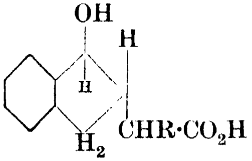
[11] *Idem*, *ibid.*, p. 674; *A.*, 18.

[12] J. Iball, *ibid.*, 1934, [*A*], **146**, 140; *A.*, 1162.

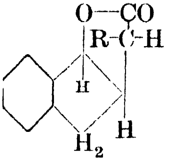
[13] W. C. Pierce, *J. Chem. Physics*, 1934, **2**, 1; *A.*, 244.

[14] (Mrs.) K. Lonsdale, *Nature*, 1934, **133**, 67; *A.*, 134.

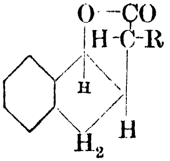
[15] K. von Auwers and O. Ungemach, *Annalen*, 1934, **511**, 152; *A.*, 889.



(I.)



(II.)



(III.)

[R = CH_2Ph]

The three forms of *cis*-cinnamic acid (melting at 68°, 58°, and 42°, respectively), so often the subject of examination, are apparently identical in solution, as shown[20] by their rates of addition of bromine, and are therefore polymorphs.

syn- and *anti-o*-Chlorobenzophenoneoximes have identical dipole moments, but in the *m*- and *p*-pairs of oximes the higher-melting form has the lower dipole moment.[21]

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[16] H. Bode, *Ber.*, 1934, **67**, [*B*], 332; *A.*, 406.

[17] M. Godchot and M. Mousseron, *Compt. rend.*, 1934, **198**, 837; *A.*, 522.

[18] R. Cornubert and P. Robinet, *Bull. Soc. chim.*, 1934, [v], **1**, 90; *A.*, 778.

[19] *J.*, 1934, 1296; *A.*, 1217.

[20] H. V. W. Robinson and T. C. James, *J.*, 1933, 1453; *A.*, 1934, 71.

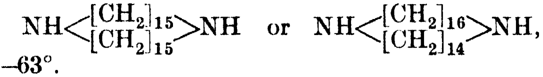
[21] G. S. Parsons and C. W. Porter, *J. Amer. Chem. Soc.*, 1933, **55**, 4745; *A.*, 1934, 131.

Many-membered Ring Compounds.—L. Ruzicka and collaborators have obtained [22] further examples of polymethylene ring compounds and their ketones up to C_{34}, and have discussed the relationships among the physical properties. The following are revised data regarding density and melting point :

No. of C atoms	20	21	22	23	24	26	28	29	30	32	34
Hydrocarbon :											
(*a*)	—	—	0·850	0·850	—	0·847	0·846	0·851	0·854	0·856	0·856
(*b*)	—	—	46°	49°	47°	43°	48°	—	57°	59°	66°
Ketone :											
(*a*)	—	0·894	—	0·890	—	—	—	0·887	0·887	—	0·885
(*b*)	59°	46°	32°	39°	36°	42°	50°	—	56°	—	64°

(*a*) density at 20°; (*b*) melting point.

The figures for the melting points are difficult to interpret, but from the densities Ruzicka deduces (*Chem. and Ind.*, 1935, **54**, 2) that the rings above C_{20} are composed of parallel double chains, the straight portions of which are identical with the *n*-paraffins in structure. This is confirmed by some *X*-ray results. However, it is to be noted that the cyclic hydrocarbons and ketones are actually denser than the corresponding normal chain compounds. A number of large ring compounds containing nitrogen have also been described,[23] *e.g.*, *cyclo*-dipentadecamethylenedi-imine,



$$NH{<}\begin{matrix}[CH_2]_{15}\\ [CH_2]_{15}\end{matrix}{>}NH \quad \text{or} \quad NH{<}\begin{matrix}[CH_2]_{16}\\ [CH_2]_{14}\end{matrix}{>}NH,$$

m. p. 62—63°.

J. W. Hill and W. H. Carothers have described [24] a number of many-membered cyclic anhydrides and cyclic esters. The anhydrides obtained by heating the acids $[CH_2]_n(CO_2H)_2$, where $n = 4$ to 12 and 16, with acetic anhydride are stated to be linear polymerides ($M = 3000$—5000) in which the unit $-O{\cdot}CO{\cdot}[CH_2]_n{\cdot}CO{\cdot}$ is repeated ; on being heated in a still, they give volatile cyclic monomeric or dimeric anhydrides, together with more complex anhydrides forming tough fibrous solids. The volatile anhydrides readily polymerise to substances which are regarded as large-ring anhydrides, resembling the so-called linear anhydrides mentioned above.

A very interesting case of a large-ring compound is provided by the phthalocyanine [25] of R. P. Linstead and collaborators. This stable substance has for its essential structural feature a 16-membered ring of 8 carbon and 8 nitrogen atoms arranged alternately in the

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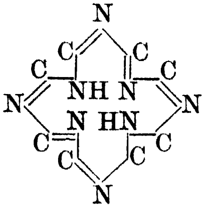
[22] L. Ruzicka, M. Hürbin, and M. Furter, *Helv. Chim. Acta*, 1934, **17**, 78; *A.*, 285.

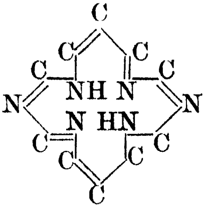
[23] L. Ruzicka, M. W. Goldberg, M. Hürbin, and H. A. Boekenoogen, *ibid.*, 1933, **16**, 1323; *A.*, 1934, 82.

[24] *J. Amer. Chem. Soc.*, 1933, **55**, 5023, 5031; *A.*, 1934, 171.

[25] C. E. Dent, R. P. Linstead, and A. R. Lowe, *J.*, 1934, 1033; *A.*, 1114.

(IV.)





(V.)

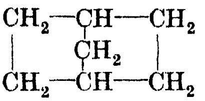
form of four cyclised pentagonal units (IV), with six double bonds. Theoretical considerations, as well as some *X*-ray evidence, indicate that this ring is flat. The copper derivative, in which the copper atom replaces the two hydrogen atoms of the imino-groups and presumably co-ordinates with the two remaining inner nitrogen atoms, is quite exceptionally stable to heat and to the action of sulphuric acid. There is thus presumptive evidence that large planar indented rings can exist without much internal strain. If the copper atom also lies in the plane of the ring, its valency distribution must presumably be planar, whereas hitherto a tetrahedral symmetry has been accepted; and similar difficulties arise regarding the distribution of the valencies to the tervalent nitrogen atoms of the imino-groups. However, as the authors point out, there is a possibility of free rotation of one of the four rings of phthalocyanine, which would have the effect of displacing an imino-group from the plane of the large ring and might therefore admit a combination with non-planar copper.

The analogy between the phthalocyanine ring system and that of the porphyrins [shown in (V)] is remarkable, and the implication is borne out by a corresponding stability in the copper derivatives. The phenomena suggest that no great difference of strain is introduced in such cyclic systems by a substitution of N$\leqslant$ for C$\leqslant$.

The possible occurrence of large planar indented rings had already been discussed [26] by the Reporter in connexion with the polymethylenes, the only case in which the values of the angles could be calculated with some confidence. It was shown that many large rings are capable of representation in axially symmetrical planar patterns, the total strain in the large rings being equal to that of simpler prototypes (*cyclo*pentane, etc.). The rings (IV) and (V), although unsaturated and not quite symmetrical, are similar in outline to some of these patterns, and are particular cases of the general scheme.

[26] H. D. K. Drew, *J. Soc. Chem. Ind.*, 1933, **52**, 538.

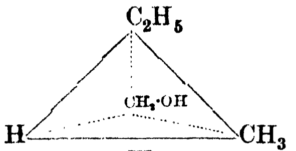
The preparation by G. Komppa and S. Beckmann (*Naturwiss.*, 1934, **22**, 171; *A.*, 658) of norbornylan (annexed formula), the parent hydrocarbon of the camphor group, is of interest from the point of view of the strain involved in bridged-ring substances where the presence of Sachse rings is probable; it melts at 86—87° and is highly volatile.



Optical Activity.—The problem of calculating optical rotatory power, never yet solved, has been brilliantly attacked by S. F. Boys,[27] who deals with the simplest case, that of a central atom surrounded by four different groups at the corners of an irregular tetrahedron. Taking the shape of the dissymmetric molecule as that determined by the close packing of four spheres, corresponding with the four different groups, about the central atom, the author shows that the magnitude of the optical rotation, as well as its sense, is completely determined by the arrangement of the refractive centres in the molecule; and develops a relatively simple formula in which the specific rotation is given in terms of the refractive index of the medium in which the rotation is measured, the total refractivities of each attached group, the radii of the groups, the wave-length of the light used, and the molecular weight of the compound. Considering the difficulty of determining the correct values for the radii of the groups in the given environment, the optical rotatory power calculated from the formula agrees remarkably well with that found experimentally for several of the simpler compounds of carbon:

	$[\alpha]_D$ calculated.	$[\alpha]_D$ experimental.
$(CH_3)(C_2H_5)CH(OH)$	9·3°	13·9°
$(CH_3)(C_2H_5)CH(NH_2)$	7·4	7·44
$(CH_3)(C_2H_5)CH(CH_2{\cdot}OH)$............	4·0	5·90
$(CH_3)(C_2H_5)CH(CH_2{\cdot}NH_2)$	3·6	5·86

The calculation gives also the absolute configuration; *e.g.*, for *l*-amyl alcohol the configuration is as shown in (VI), where $CH_2{\cdot}OH$ is represented as at the apex of a tetrahedron whose base rests below on the plane of the paper. It is pointed out that, if one group can be changed whilst the compound retains the same configuration, the sign of the optical rotation should change when the effective radius is increased above that of the next largest group. This agrees with experience; *e.g.*, amyl alcohol and amylamine are of opposite rotatory sign to all compounds prepared by substituting another group (not hydrogen) for the OH group, since OH and NH_2 are the only radicals



(VI.)

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[27] *Proc. Roy. Soc.*, 1934, [*A*], **144**, 655, 675; *A.*, 832.

which have smaller atomic volumes than the CH_3 group; all other radicals cause the CH_2X group to be larger than the adjacent $CH_2\cdot CH_3$ group.

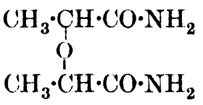
A formula connecting rotatory dispersion with the nature of the groups is also given; and the temperature effect is shown to be due only to variations in the properties of the medium.

These papers, if capable of withstanding expert criticism, would contain the solution to many outstanding chemical problems, notably that of the Walden inversion, and would therefore form a welcome contribution to knowledge.

In connexion with the above, it may be noted that, according to D. H. Brauns,[28] the specific rotations of the 1-halogeno-2-methylbutanes (fluoro-, chloro-, bromo-, and iodo-) are approximately in the same ratio as the atomic diameters of the (neutral) halogen atoms.

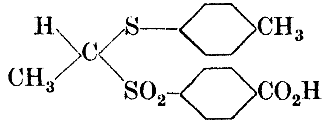
The following optical resolutions of interesting forms of substances may be grouped together:

(1) The *dl*-form of dilactyldiamide (VII) is spontaneously resolved [29] by crystallisation from water above about 35°.

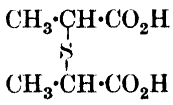


$$\begin{array}{c} CH_3\cdot CH\cdot CO\cdot NH_2 \\ | \\ O \\ | \\ CH_3\cdot CH\cdot CO\cdot NH_2 \end{array}$$

(VII.)



(VIII.)



$$\begin{array}{c} CH_3\cdot CH\cdot CO_2H \\ | \\ S \\ | \\ CH_3\cdot CH\cdot CO_2H \end{array}$$

(IX.)

(2) *dl*-α-*p*-Carboxybenzenesulphonyl-α-*p*-tolylthiolethane (VIII) is resolved [30] by means of a half-equivalent of *l*-menthylamine; the *d*-acid has $[\alpha]_{5461} + 130^\circ$ in chloroform, but gives an inactive sulphone on oxidation.

(3) The resolution of *dl*-erythronic acid has been completed[31] by means of brucine and quinine; the lactones have $[\alpha]_D \pm 73^\circ$.

(4) *dl*-Histidine monohydrochloride is spontaneously resolved [32] on rapid crystallisation, its behaviour recalling that of atropine sulphate (*A.*, 1928, 653).

(5) *dl*-β-Thiodipropionic acid (IX) is resolved[33] by means of quinine; the acids have $[\alpha]_D$ about $\pm 200^\circ$.

(6) *l*-Allantoin, having $[\alpha]_D^{20^\circ} - 92^\circ\ 24'$ (in water), has been

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[28] *J. Amer. Chem. Soc.*, 1934, **56**, 1421; *A.*, 866.

[29] P. Vièles, *Compt. rend.*, 1934, **198**, 2102; *A.*, 876.

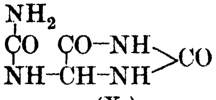
[30] F. B. Kipping, *J.*, 1933, 1506; *A.*, 1934, 71.

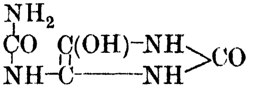
[31] J. W. E. Glattfeld and L. R. Forbrich, *J. Amer. Chem. Soc.*, 1934, **56**, 1209; *A.*, 757.

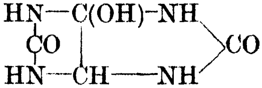
[32] R. Duschinsky, *Chem. and Ind.*, 1934, 10; *A.*, 196.

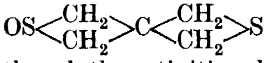
[33] A. Fredga, *Svensk Kem. Tidskr.*, 1934, **46**, 10; *A.*, 393.

obtained [34] from inactive allantoin by means of the allantoinases from soya-bean and from skate liver, which preferentially hydrolyse the *d*-form; *l*-allantoin racemises quickly in neutral or alkaline solution; the possibility of optically active tervalent nitrogen being ruled out, the classical molecule (X) must be present (compare the remaining formulæ which are symmetrical in the keto-form).


(X.)





(7) The resolution of 2 : 6-dithia*spiro*heptane 2 : 6-dioxide,  $OS<^{CH_2}_{CH_2}>C<^{CH_2}_{CH_2}>SO$, which is of the "allenic type," is claimed,[35] though the activities observed were small.

(8) A claim has been made that *o*-toluidine-3 : 5-disulphonic acid is resolvable [36] by means of strychnine. It may be noted here that the existence of di-*o*-isomerides in benzene, due to supposed fixation of the Kekulé double bonds (see *A.*, 1927, 47), has recently been challenged.[37]

J. Clark and J. Read have described [38] novel methods of preparing *d* (and *l*)-borneol by crystallising impure *d*-bornyl *d*-bornoxyacetate, and of resolving *dl*-menthol by esterifying it with *l*-menthylglycine and fractionating the resulting diastereoisomeric pair; *l*-menthylglycine appears to be a valuable addition to the available optically active acids.

The asymmetric arsenic atom. The only convincing example of an optically active compound of quinquevalent arsenic has hitherto been the *p*-carboxyphenylmethylethylarsine sulphide of Mills and Raper (*J.*, 1925, **127**, 2479), but G. Kamai [39] now reports an apparent resolution of *p*-tolylbenzylethyl-*n*-propylarsonium iodide, of which the *d*-form, with $[\alpha]_D^{5^\circ} + 9{\cdot}86^\circ$ in acetone, was obtained; it rapidly became inactive. An observed angle of rotation of $+ 0{\cdot}22^\circ$ is recorded. This substance differs, of course, from the sulphide in that it is a true arsonium salt.

Tervalent arsenic compounds have not hitherto been resolved. C. F. H. Allen, F. B. Wells, and C. V. Wilson [40] now report the fractionation of the *d*-bromocamphorsulphonate of the benzophenarsazine (XI); the values of the rotatory power of the arsenic radicals, calculated from the values for the separated salts, were $[\alpha]_D^{25°}$ − 24·9° and + 25·6°, respectively, in 95% alcohol. However, the active chloroarsazines could not be obtained. The possibility of active tervalent nitrogen being neglected, the results, so far as they go, point to the tetrahedral symmetry of tervalent arsenic.

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[34] R. Forse, P. E. Thomas, and P. de Groeve, *Compt. rend.*, 1934, **198**, 689, 1374; *A.*, 534, 695.

[35] H. J. Backer and K. J. Keuning, *Rec. trav. chim.*, 1934, **53**, 798; *A.*, 901.

[36] A. Sementzov, *Ukraine Chem. J.*, 1933, **8**, 193; *A.*, 1934, 763.

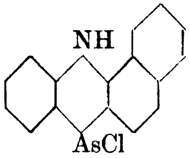
[37] A. Contardi and A. Dansi, *Rend. R. Ist. Lombardo Sci. Lett.*, 1933, [ii], **66**, 203; *A.*, 1934, 177.

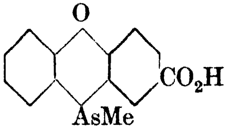
[38] *J.*, 1934, 1773, 1775.

[39] *Ber.*, 1933, **66**, [*B*], 1779; *A.*, 1934, 197.

[40] *J. Amer. Chem. Soc.*, 1934, **56**, 233; *A.*, 312.

(XI.)



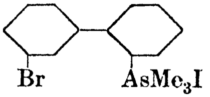


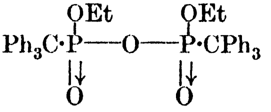
(XII.)

(Miss) M. S. Lesslie and E. E. Turner [41] have obtained a much more definite resolution of a phenoxarsinecarboxylic acid (XII) by means of strychnine, the liberated *d*- and *l*-acids having $[\alpha]_{5461}^{20°}$ ± 111·5° in alcohol. However, the authors incline to attribute the activity, not to asymmetry of tervalent arsenic, but to a folding of the molecule about the axis O . . . As, whereby it becomes diplanar and therefore dissymmetric.

The same authors [42] recently obtained evidence of dissymmetry in the arsonium salt (XIII), although the angle of rotation observed here was only 0·12° ($\lambda = 5461$). In this case they attributed the lack of symmetry to restriction of rotation of the phenyl groups about the common bond, in accordance with current ideas.

(XIII.)





$$\mathrm{Ph_3C{\cdot}\overset{OEt}{\underset{\overset{\downarrow}{O}}{P}}{-\!\!-}O{-\!\!-}\overset{OEt}{\underset{\overset{\downarrow}{O}}{P}}{\cdot}CPh_3}$$

(XIV.)

H. H. Hatt has described [43] the *meso*- and racemic forms of ethyl triphenylmethylpyrophosphonate (XIV), apparently the only case of isomerism due to two structurally similar asymmetric phosphorus atoms; both esters give the same acid on hydrolysis owing to resonance.

Optically active diphenylbenzene derivatives. Where there are two centres of restricted rotation the same effect is produced as if there were two asymmetric centres in the molecule; hence in structurally symmetrical molecules we should expect to find *meso*- and racemic forms. This has been realised [44] in the forms (XV) and (XVI), the second only being resolvable, since the first has a centre of symmetry. The active forms of (XVI) had $[\alpha]_D^{25^\circ}$ − 16·2° and + 13·4° in ethyl acetate. Reversible oxidation to an active quinone of opposite rotatory sign without any racemisation was found to be possible.

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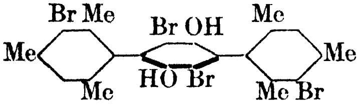
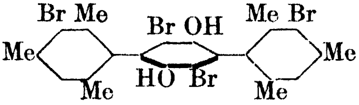
[41] *J.*, 1934, 1170; *A.*, 1118. [42] *J.*, 1933, 1588; *A.*, 1934, 181.

[43] *Ibid.*, p. 776; *A.*, 1933, 962.

[44] A. E. Knauf, P. R. Shildneck, and R. Adams, *J. Amer. Chem. Soc.*, 1934, **56**, 2109.



(XV.)



(XVI.)

Metallic Complexes containing Organic Radicals.—(a) *Resolution of octahedral cadmium salts.* The optical activation of triethylenediaminocadmium chloride, $[Cd\ en_3]Cl_2$, of the sulphate, and of several other corresponding salts has been effected by P. Neogi and G. K. Mukherjee,[45] by making use of the acidic property of nitrocamphor. Only one active form of each salt was produced, and the active salts racemised rapidly even in the solid state. The active chloride had $[\alpha]_D^{30^\circ}$ + 113·7° in water. Similar optically active octahedral zinc complexes have been prepared by the authors.

In such cases as the above, where only one enantiomorph of a readily inactivated substance is producible by the use of a single resolving agent, it would seem almost open to question whether any information as to the normal symmetry of the substance is obtained, for the optical activation might be the result of a temporary distortion of the substance by the resolving agent, normal symmetry being reassumed, after an interval, on removal of the latter; the enantiomorph of the first resolving agent would produce an equal and opposite distortion. A comparison of the magnitude of the effects of several different resolving agents might, however, give the required information. In those members of the diphenyl series which are readily inactivated, an effect of the kind suggested seems actually to occur.[46]

(b) *Isomerism among derivatives of palladium and platinum.* A. A. Grünberg and V. M. Schulman have described [47] the first members to be discovered of the β-series of palladodiammines, formerly confused with the pink series of pallado-salts of the palladotetrammines. As had already been predicted,[48] these yellow substances are relatively unstable, passing into the corresponding α-isomerides. The β-isomerides described, which can be obtained only from the acetates of the amines, are $Pd(NH_3)_2Cl_2$, $Pd(C_5H_5N)_2Cl_2$, and the corresponding bromides.

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[45] *J. Indian Chem. Soc.*, 1934, **11**, 225; *A.*, 640.

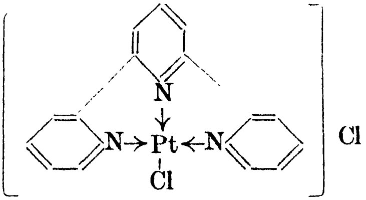
[46] Compare W. Brydówna, *Rocz. Chem.*, 1934, **14**, 304; *A.*, 1011; M. S. Lesslie and E. E. Turner, *J.*, 1934, 347; *A.*, 538; M. S. Kharasch, J. K. Senior, D. W. Stanger, and J. A. Chenicek, *J. Amer. Chem. Soc.*, 1934, **56**, 1646; N. E. Searle and R. Adams, *ibid.*, p. 2112.

[47] *Compt. rend. Acad. Sci.*, *U.R.S.S.*, 1933, 218; *A.*, 1934, 379.

[48] H. D. K. Drew, F. W. Pinkard, G. H. Preston, and W. Wardlaw, *J.*, 1932, 1895; H. D. K. Drew and G. H. Wyatt, *J.*, 1934, 56; *A.*, 284.

The stereochemical relationships among the α- and β-series of disulphines and diammines of platinum and of palladium have now been determined. The α-disulphines of platinum are *trans*-forms and correspond stereochemically and structurally with the α-diammines, and not with the β-diammines as was supposed by Werner. For details of this rather complicated subject the original papers [49] must be consulted.

The type of valency distribution present in palladous and platinous compounds in which the metal is associated with four groups or atoms has been the subject of much work. Recent investigations have shown, with little remaining doubt, that the arrangement is always, or nearly always, planar. F. S. H. Head and the Reporter obtained [50] well-defined *cis*- and *trans*-forms of each of the following platotetrammines: [Pt am ae ib]Cl_2 and [Pt ib_2]Cl_2, where am = NH_3, ae = NH_2Et, and ib = $NH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}NH_2$. A. A. Grünberg and P. Ptizyn, and F. W. Pinkard, E. Sharratt, W. Wardlaw, and E. G. Cox, have reported [51] *cis*- and *trans*-isomerides of diglycine-platinum, $Pt(NH_2{\cdot}CH_2{\cdot}CO_2)_2$, where the carboxyl is presumably not ionised from platinum. G. T. Morgan and F. H. Burstall have prepared [52] red and black forms of the soluble triammine, [Pt trp Cl]Cl, where trp = 2 : 2′ : 2″-tripyridyl, either of which, if monomeric, must be of planar symmetry (XVII). B. N. Dickinson has likewise shown [53] the planar structure of the palladotetrammine, $Pd(NH_3)_4Cl_2,H_2O$, by means of *X*-rays, in agreement with the previous work of E. G. Cox. F. P. Dwyer and D. P. Mellor have isolated [54] two forms of palladium bis-*anti*benzylmethyldioxime,



(XVII.)

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[49] H. D. K. Drew and G. H. Wyatt, *J.*, 1934, 56; *A.*, 284; H. Saenger and W. Wardlaw, *ibid.*, p. 182; *A.*, 397.

[50] *Ibid.*, p. 221; *A.*, 397.

[51] *J. pr. Chem.*, 1933, **136**, 143; *J.*, 1934, 1012; *A.*, 994.

[52] *J.*, 1934, 1498.

[53] *Z. Krist.*, 1934, **88**, 281; *A.*, 1161.

[54] *J. Amer. Chem. Soc.*, 1934, **56**, 1551; *A.*, 945.

one of which should be dissymmetric on the basis of a pyramidal valency distribution; no resolution was effected. Claims of the resolution of compounds of 4-covalent palladium, platinum, and nickel have been made by Rosenheim, Reihlen, and others, whose results still remain unreconciled. H. D. K. D.

Long-chain Unsaturated Aliphatic Acids.

C. R. Noller and R. A. Banneret [55] have synthesised oleic acid and elaidic acid from 9-chlorononaldehyde prepared from heptadecenyl chloride (from oleyl alcohol), using Shoemaker and Boord's method.[56] The acid obtained consisted of 63% of elaidic acid and 37% of oleic acid.[57] This is considered to be the first complete synthesis of elaidic and oleic acids. Contributions to the constitution of higher unsaturated acids are given by Y. Inoue and K. Sahashi [58] in their examination of clupanodonic acid, and to the polymerisation of its methyl ester by K. Kino,[59] who has examined the products of ozonolysis of the intramolecular reaction product of the methyl and the butyl ester, giving $CO_2H{\cdot}C_9H_{14}{\cdot}CO_2Bu$, which orients the ester grouping with respect to one double linking. The other products of ozonisation are explained by a new formula for methyl clupanodonate.

J. S. Long, A. E. Rheineck, and G. L. Ball [60] have continued their researches on the drying of linseed oil, using trilinolenic glyceride. They find the oxygen absorbed corresponds to 2O for each double linkage with the formation of polar molecules. The second stage is the association of polar molecules to form gels. The ageing of linseed oil or trilinolenic glyceride consists in the gradual transition of polar liquid phase to a solid phase of substantially the same ultimate analysis. S. Goldschmidt and K. Freudenberg [61] have examined the oxidation of linolenic acid and its methyl ester by oxygen in the presence of a cobalt catalyst. The formation of peroxides is not accompanied by the development of acidic groups, and all the linolenic acid has disappeared when 2 molecules of oxygen are absorbed. The peroxides are very stable and the peroxide value remains constant for many days. Consideration of these two papers shows the stress laid in the one case on peroxides and, in the other, on association of the keto-enol modifications of the same peroxide causing passage from the fluid to the solid state. From the Reporter's unpublished investigation on the oxidation of α- and β-elæostearic acids or their glycerides combined with maleic anhydride, the formation of both peroxides and keto-enol groups takes place depending on the position of the double linkages in the molecule. The association is marked in the peroxide groups and is favoured by solvents of low dielectric constants. The results are in confirmation of those obtained from the oxidation of β-elæostearic acid from tung oil.[62] The association of the oxidation products of drying oils is to be looked for at the remote double linkages, which seem to be capable of yielding peroxides on oxidation. In investigations of the above character it is of importance to have reliable methods for the estimation of the groups formed by the oxidation, *e.g.*, peroxide, hydroxyl, keto, etc. Improvements in the estimation of hydroxyl values of acid substances have been made by E. S. West, G. Hoagland, and G. H. Curtis.[63] The previous methods were applicable only to esters.

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[55] *J. Amer. Chem. Soc.*, 1934, **56**, 1563; *A.*, 991.

[56] *Ibid.*, 1931, **53**, 1505; *A.*, 1931, 709.

[57] H. N. Griffiths and T. P. Hilditch, *J.*, 1932, 2315; *A.*, 1932, 1111.

[58] *Proc. Imp. Acad. Tokyo*, 1932, **8**, 371; *A.*, 1933, 145.

[59] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1933, **21**, 63; 1934, **24**, 218; *A.*, 1933, 807; 1934, 1202.

[60] *Ind. Eng. Chem.*, 1933, **25**, 1056; *B.*, 1933, 1016.

[61] *Ber.*, 1934, **67**, [*B*], 1589; *A.*, 1200.

Spectroscopic study of the elæostearic acids from tung oil shows that the absorption spectra of the α- and the β-form differ sufficiently for identification, so that the composition of a mixture can be determined.[64]

The absorption of oxygen by linseed oil in the presence of catalysts [$K_3W(CN)_8$, $K_3Mo(CN)_8$, and $K_3Fe(CN)_6$] has been examined by B. F. Chow and S. E. Kamerling,[65] who found that the rate of absorption was in the decreasing order from the first-named, and gave an empirical equation relating the rate of oxygen absorption to the oxidation potential. In the case of oleic acid oxygen is necessary for the reduction of the ferricyanides in HPO_4'' buffer, 5—6 molecules of O being required for the reduction of 2 molecules of ferricyanide. Acetoxime was a marked inhibitor of the oxygen absorption.

N. A. Milas's [66] view is that in all autoxidations the atoms to which the oxygen molecule is initially added make definite contributions of 2 electrons; metastable peroxides of high instability and energy content are formed and may revert to ordinary peroxides by transferring their excess energy to other molecules, or may initiate oxidation of other molecules.[67] The observed separation of peroxide from a benzene solution of a drying oil is assisted by previous passage of the oxygen through the glyceride solution and indicates activation of gas in the solution.

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[62] R. S. Morrell and S. Marks, *J. Soc. Chem. Ind.*, 1931, **50**, 27T; *B.*, 1931, 549.

[63] *J. Biol. Chem.*, 1934, **104**, 627; *A.*, 510.

[64] A. Dingwall and J. C. Thompson, *J. Amer. Chem. Soc.*, 1934, **56**, 899; *A.*, 631.

[65] *J. Biol. Chem.*, 1934, **104**, 69; *A.*, 261; B. F. Chow, *J. Amer. Chem. Soc.*, 1934, **56**, 894; *A.*, 607.

[66] *J. Physical Chem.*, 1929, **33**, 1204; 1934, **38**, 411; *A.*, 1929, 1019; 1934, 607.

The " bloom " of a number of paint and varnish films has been correlated with their contact angles with water.[68] Films with contact angles below 65° show the defect of " bloom "; between 65° and 90° the films do not condense water. Examination of the maleic anhydride compounds [69] of α- and β-clæostearin by the above method has shown that the β-films are active and the α-compounds are not.[70] This attractive power is considered to be dependent on the surface concentration of the active peroxides and their increased association diminishes the attraction. A. H. Hughes [71] has shown that the surface potentials of unimolecular films of α- and β-elæostearic acid–maleic anhydride compounds are markedly different and the unsaturated linkage of the β-compound increases the surface potential. The position of the oxidisable double linkage is important, because it is known that the β-compound is more easily oxidised and associated, whereas the α-compound oxidises with difficulty and does not give an active peroxide.

A. H. Hughes [72] has also examined the unimolecular films of long-chain aliphatic compounds on aqueous solutions by surface-pressure and surface-potential methods in the series oleic, petroselic, and Δ^{α}-*iso*oleic acids, and has found that the dipole system of the double linking has a marked effect on the adhesion to the water surface and that proximity to a carboxyl group increases the dipole moment. The dipole moment of chaulmoogric acid containing a five-membered ring is greater than that of a double linking in a straight chain; a triple linking has a dipole moment greater than that of a double linking and causes greater adhesion to the surface. A. H. Hughes and E. K. Rideal [73] have determined the rate of oxidation of the above acids, as well as of α- and β-elæostearic acids, by measurement of the change of surface potential with time. The reaction velocity decreases with the compression of the film and depends on the accessibility of the double linking to the oxidising agent and is also affected by the position of the double linking in relation to the polar carboxyl group.

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[67] Compare H. N. Stephens, *J. Physical Chem.*, 1933, **37**, 209; 1934, **38**, 419; *A.*, 1933, 61; 1934, 607.

[68] N. K. Adam and R. S. Morrell, *J. Soc. Chem. Ind.*, 1934, **53**, 255T; *B.*, 931.

[69] R. S. Morrell, S. Marks, and H. Samuels, *ibid.*, 1933, **52**, 130T; *B.*, 1933, 556.

[70] N. K. Adam and R. S. Morrell, *ibid.*, 1934, **53**, 255T, 260T; *B.*, 931.

[71] *J.*, 1933, 338; *A.*, 1933, 565.

[72] *Loc. cit.*

[73] *Proc. Roy. Soc.*, 1933, [*A*], **140**, 253; *A.*, 1933, 679.

The structural investigation of these long-chain unsaturated aliphatic esters and acids, combined with observations on their surface properties as instanced by the work of Hughes and Rideal, will throw much light on many of the difficult problems of the acids and esters which are met with in industry.

Polymerisation of Long-chain Aliphatic Compounds.

In paints and varnishes the consideration of micellar colloids is favoured by some workers in contrast with the molecular colloid aspect advocated by Staudinger. A survey on these lines puts forward paint and varnish systems as containing micelles of molecules held together by primary valencies or adhesional forces according to chance contact, the temperature of the system exerting considerable influence; *e.g.*, at 180° glycerol and phthalic anhydride give a soft gelling resin mainly of straight-chain growth, but at 260° the product is brittle because cross linking (primary valencies) of the pre-formed molecular chains becomes more frequent in consequence of the activity of the β-C atom in the glycerol molecule. The sudden increase in the rate of gelation of tung oil at 270° and the brittleness of the product are similarly explained.[74] In a later communication [75] the ideas are developed to include the influence of free fatty acids, resins, driers, and pigments as dispersing or coagulating agents. The peculiar characteristics of tung oil films are stated to be due to random coagulation of large flocculates or to a partial orientation. " Blooming " is ascribed to swelling of flocculants by absorption of water.

H. Freundlich [76] considers resins as gels of highly polymerised substances, the disperse phase consisting of a more highly polymerised form of the material composing the continuous phase, and the plastic behaviour is parallel to that of glasses and is determined mainly by the viscosity of the continuous phase, the disperse phase being of secondary importance; *i.e.*, they are two-phase colloids. For the development of plasticity with its variable coefficient of viscosity and possibly yield value, some affinity between solid and liquid is essential. The phenomenon of thixotropy frequently met with in plastic masses and associated with loose packing of the particles demands attractive forces between the latter of the van der Waals order. The above may be taken as the purely colloidal aspect; which correlates many phenomena successfully, especially those of comparatively simple structure, but structure is of great importance (cf. the properties and structure of bentonite and kaolinite) and it is of equal importance in consideration of properties of oil films and resins. The neglect of investigation into the structure and molecular arrangement of long-chain unsaturated oils and acids has introduced uncertainty concerning behaviour on oxidation and polymerisation. There is need for co-ordination of the two aspects, because adequate knowledge of each is essential.

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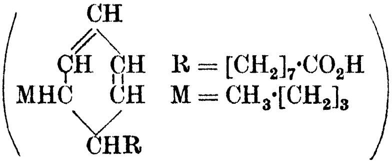
[74] W. E. Wornam, *J. Oil and Col. Chem. Assoc.*, 1933, **16**, 231; *B.*, 1933, 79.

[75] *Idem, ibid.*, 1934, **17**, 119; *B.*, 510.

[76] *J. Soc. Chem. Ind.*, 1934, **53**, 218T.

The polymeric molecules may assume a linear form of repeated units, or a branch form which will lead ultimately to the building up of a solid three-dimensional molecular structure (cross-linked polymerisation). In condensation polymerisation a third substance is eliminated (usually water) as a result of chain formation.[77] The apposition of chain polymerised molecules to form fibres may be produced by flow and shear, whereby a thread of glassy polyester is instantaneously converted by strain into an oriented fibre (J. W. Hill and W. H. Carothers).[78] These linear ω-polyesters have been obtained from dibasic acids and glycols heated in a molecular still to give tough opaque solids. The cross-linked form of polymeride is more difficult to investigate, the simplest representation being silicic acid. In long-chain unsaturated acids glyceride association of double linkages may proceed to a four-ring dimeride, for which there is yet no conclusive evidence. E. Rossman[79] concludes that below 300° elæostearic acid does not pass beyond a dimeride and has isolated a *cyclo*monoelæostearic acid and *cyclo*dielæostearic acid.



$R = [CH_2]_7{\cdot}CO_2H$ $M = CH_3{\cdot}[CH_2]_3$

The isomerism of elæostearic acid into the cyclic form is stated to be irreversible. In strongly heated tung oils further *cyclo*polymerides are formed which cannot be depolymerised by heat (Rossman). The production of dibasic acid with the loss of one double linkage has been suggested by L. A. Jordan[80] as occurring in the first stage of the polymerisation. Further investigation is advisable, because the results of Rossman and Jordan are not in general agreement with the behaviour of maleic anhydride compounds from α- and β-elæostearic acid. W. Chalmers,[81] in a discussion on macropolymerisation reactions, criticises a stepwise reaction mechanism and supports a polymerisation chain mechanism involving (1) primary activation of the monomeride and (2) a subsequent process of concatenation which is rendered possible by the presence of free terminal bonds on all intermediate stages. The linking of the monomeric units proceeds initially at a rate almost instantaneous compared with that of activation, but for very great chain lengths the rate becomes increasingly slow. There is experimental evidence in support of the above, but further work is necessary to decide on the relative activities of the unsaturated double linkages, because the adoption of the dimeride view has as yet inadequate confirmation.

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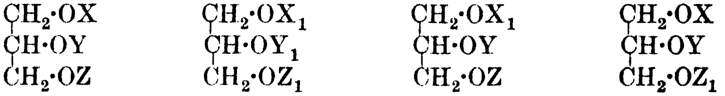
[77] W. H. Carothers and collaborators, *J. Amer. Chem. Soc.*, 1929, **51**, 2548, 2560; 1930, **52**, 314, 711, 3292; *A.*, 1929, 1165; 1930, 319, 452, 1272.

[78] *Ibid.*, 1933, **55**, 5023; *A.*, 1934, 171.

[79] *Fettchem. Umschau*, 1933, **40**, 96, 117; *A.*, 1933, 807.

[80] *J. Oil and Col. Chem. Assoc.*, 1934, **17**, 47; *B.*, 333.

In the polymerisation of glycerides by heat it has been suggested that an interchange of ester groupings takes place slowly until the temperature reaches 260°. The mixed unsaturated glycerides may



$$\begin{array}{cccc} CH_2{\cdot}OX & CH_2{\cdot}OX_1 & CH_2{\cdot}OX_1 & CH_2{\cdot}OX \\ | & | & | & | \\ CH{\cdot}OY & CH{\cdot}OY_1 & CH{\cdot}OY & CH{\cdot}OY \\ | & | & | & | \\ CH_2{\cdot}OZ & CH_2{\cdot}OZ_1 & CH_2{\cdot}OZ & CH_2{\cdot}OZ_1 \end{array}$$

(where X, Y, Z, X_1, Y_1, Z_1 are different fatty radicals in the glycerides)

associate at different rates, and at higher temperatures and shorter times of heating the iodine value may even be higher than after longer times of heating at lower temperatures. The ester interchange between tristearin and tripalmitin has been criticised by T. Malkin[82] and J. C. Smith,[83] who have shown that palmitic and stearic ethyl or glyceryl esters are dimorphous. From *X*-ray examination, Malkin concludes that the triglycerides from tridecoin to tristearin exist in three forms; the stable β-form with the high m. p. has long C chains tilted across planes formed by terminal methyl groups, whereas in the α-form they are perpendicular to these planes. He favours a T formula for glycerides rather than an E arrangement. This interchange of esters, which seems unlikely from Malkin's work, can only be very partial in the heat polymerisation of linseed oil and would not explain the separation of stearic and palmitic acids and a modification of oleic acid from the acetone-insoluble portion of the oil.[84]

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[81] *J. Amer. Chem. Soc.*, 1934, **56**, 912; *A.*, 607.

[82] *Trans. Faraday Soc.*, 1933, **29**, 977; *A.*, 1933, 1107; *J.*, 1931, 2796; *A.*, 1932, 327; *J.*, 1934, 671.

[83] *J.*, 1931, 802; *A.*, 1931, 684.

[84] R. S. Morrell, *J. Soc. Chem. Ind.*, 1915, **34**, 107T.

Condensation Polymerisation.

W. H. Carothers and F. J. van Natta [85] have prepared from ι-hydroxydecoic acid a series of polyesters (*M* 2780—25,200) of the type $OH\cdot([CH_2]_9\cdot CO\cdot O)_n\cdot[CH_2]_9\cdot CO_2H$. Strong oriented fibres are obtained only from esters of molecular weight greater than 9330.[86]

J. W. Hill and W. H. Carothers [86] have produced from the acids $[CH_2]_n(CO_2H)_2$ ($n = 4$—12 and 16), by heating with acetic anhydride, linear polymerides of α-anhydrides (*M* 3000—5000) of the type $\cdot O\cdot CO\cdot[CH_2]_n\cdot CO\cdot O\cdot CO\cdot[CH_2]_n\cdot CO\cdot O\cdot CO\cdot[CH_2]_n\cdot CO\cdot$. In the molecular still, volatile β-anhydrides (fluid cyclic monomerides or crystalline dimeric anhydrides) and more complex ω-anhydrides are produced, which are tough opaque solids capable of being drawn into pliable highly oriented films; these, when heated long enough in the molecular still, are converted into β-anhydrides. When linear polyesters of unit length greater than 7 are heated at 200—250° under conditions of molecular distillation, the chains couple to form longer chains. The polyesters (*M* 10,000) can be drawn into tough pliable forms. It was recognised that depolymerisation by ester interchange might occur in the molecular still as in the case of six-membered cyclic esters.[87]

Polymeric methylene carbonates prepared from $(CH_2)_n(OH)_2$ ($n = 5$, 7—9, 11—14, and 18), butyl carbonate, and a little sodium at 170° are depolymerised by heating with catalysts [88] in a vacuum and under certain conditions smooth depolymerisation to the corresponding monomerides or dimeric esters occurs: the method makes it possible to obtain for the first time monocyclic esters in good yields. The macrocyclic esters and anhydrides of the two preceding papers have odours of musk-like character resembling those of ketones and lactones of the same ring size. The rings in the neighbourhood of 15 atoms all have musk-like odours.[89] The formation of large ring ketones is considered to involve the intermediate production of a linear polyketone, which then decomposes; the changes are similar to those for esters and anhydrides (above). Rings of more than 5 atoms are not regarded as strainless and the probable nature of the strain in large rings is discussed.[90] Bifunctional esterifications generally yield cyclic monomerides or linear polyesters depending on the reactant (most important), the nature of the unit, and the experimental conditions, especially dilution. It is well known that substituents (*e.g.*, methyl) favour ring closure. The simplest possible structural situation for self-esterification is found in the ω-hydroxy-acids, which have been investigated for the first time; ε-hexolactone has been prepared and its behaviour compared with that of other cyclic or polyesters.[91] E. O. Craemer and W. D. Lansing[92] have subjected polymeric ω-hydroxydecoic acid (*M* 25,220) in *s*-tetrabromoethane solution to ultra-centrifugal analysis. The molecular weight deduced from the specific sedimentation is much too low and the value calculated from the diffusion coefficient is much too high. The value calculated from the sedimentation equilibrium agrees fairly well with the above. The authors state their views as to limitation of ultra-centrifugal analysis.

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[85] *J. Amer. Chem. Soc.*, 1933, **55**, 4714; *A.*, 1934, 56.

[86] *Ibid.*, pp. 5023, 5031, 5039, 5043; *A.*, 1934, 171.

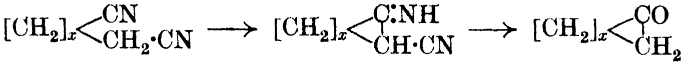
[87] W. H. Carothers, G. L. Dorough, and F. J. van Natta, *ibid.*, 1932, **54**, 761; *A.*, 1932, 366.

[88] J. W. Hill and W. H. Carothers, *loc. cit.*

[89] *Loc. cit.*, see ref. 86.

[90] J. W. Hill and W. H. Carothers, *loc. cit.*

In most instances, only small yields of cyclic ketones containing many carbon atoms are obtainable by Ruzicka's method, owing to the tendency of the reactants to polymerise. A new method has been developed[93] which to some extent overcomes these difficulties. For example, when a normal aliphatic dinitrile and an alkali-metal derivative of a secondary amine are allowed to react in high dilution, a cyano-ketimine is produced in good yield, from which the cyclic ketone is readily obtained by acid hydrolysis:



$$[CH_2]_x{<}\begin{matrix}CN\\CH_2\cdot CN\end{matrix} \longrightarrow [CH_2]_x{<}\begin{matrix}C{:}NH\\CH\cdot CN\end{matrix} \longrightarrow [CH_2]_x{<}\begin{matrix}CO\\CH_2\end{matrix}$$

M. Wadano, C. Trogus, and K. Hess,[94] put forward the view that the oxygen linkages in polymeric CH_2O are of the same character as in esters, amides, and semi-acetals and the mechanism of the polymerisation and depolymerisation in water is similar to that of the rupture and formation of such linkings. I. Sakurada[95] states that there is a fundamental difference between viscosity properties of natural and synthetic polymerides and Staudinger's viscosity rule is not applicable to substances such as cellulose, starch, and caoutchouc. He has determined the viscosity of a number of synthetic and natural polymerides according to his own special formula. Another critic of Staudinger's viscosity rule is A. J. Wildschut.[96] The application of Staudinger's viscometric method is not valid for natural rubber, but holds for synthetic and plasticised natural rubber. H. Staudinger[97] has replied to his critics and defends strongly the validity of the viscometric method.

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[91] F. J. van Natta, J. W. Hill, and W. H. Carothers, *J. Amer. Chem. Soc.*, 1934, **56**, 455; *A.*, 392.

[92] *Ibid.*, 1933, **55**, 4319; *A.*, 1933, 1276.

[93] K. Ziegler *et al.*, *Annalen*, 1933, **504**, 94; *A.*, 1933, 951; *Ber.*, 1933, **66**, [*B*], 1867; *A.*, 1934, 195; *Annalen*, 1934, **511**, 1; *A.*, 894.

[94] *Ber.*, 1934, **67**, [*B*], 174; *A.*, 493.

[95] *Ibid.*, p. 1045; *A.*, 870.

[96] *Rec. trav. chim.*, 1933, **52**, 935; *A.*, 1933, 1300.

Polymerisation of Unsaturated Aliphatic Hydrocarbons.

The polymerisation of acetylene has been studied by G. Mignonac and E. Ditz,[98] who have found that at 75° the products are benzene and a fluid polymeride, C_4H_4 (b. p. 7°), which on fractionation gives a yellowish-green polymeride (chlorene). F. Toul[99] discusses the catalysis of acetylene polymerisation in mercury vapour light. W. Kemula and S. Mrazek,[1] from absorption spectrum measurements, have shown that benzene, C_4H_4, and derivatives of $C_{10}H_8$ are formed during the polymerisation of acetylene. The preparation of vinylacetylene, CH_2:CH·C:CH, from αδ-butylene dibromide by Willstätter and Wirth's method is communicated by E. A. Shilev, A. N. Makashina, A. E. Smirnova, and G. I. Yakimov.[2] The polymerisation of vinylacetylene at 105° in steel bombs gives hydrocarbons, $C_{12}H_{22}$, $C_{16}H_{28}$, and $C_{20}H_{34}$, which are considered to be *cyclo*butane derivatives. In the presence of acids at 105° vinylacetylene yields styrene but not polystyrene.[3] The mercury derivatives of vinylacetylene and also the α-halogeno-β-vinylacetylene are described by W. H. Carothers, R. A. Jacobson, and G. Berchet.[4] R. A. Jacobson, H. B. Dykstra, and W. H. Carothers have found that vinylacetylene and alcohols in the presence of sodium alkoxide (NaOR) give $C(CH_3)$:C·CH_2·OR and describe the methyl, benzyl, and other ethers.[5] M. E. Cupery and W. H. Carothers[6] have investigated the polymerides of divinylacetylene. When divinylacetylene is heated for several hours at its boiling point (85°), out of contact with the air, it is polymerised to a viscous oil (synthetic drying oil); about 8% is polymerised in 3 hours at 80° to give a dimeride (*M* 230), which is *trans*-1 : 2-divinylethynyl*cyclo*butane. A trimeride, bisvinylethynyl*cyclo*butylacetylene, is also a polymerisation product. N. D. Zelinski, Y. L. Donisenko, N. S. Evantova, and S. I. Khromov[7] have examined the polymerisation of butadiene, isoprene, dimethylbutadiene, and *cyclo*hexadiene in contact with aluminium chloride. W. E. Vaughan[8] has shown that the polymerisation of isoprene, between 286° and 571°, is a bimolecular association reaction and one molecule of dimeride is obtained for every 530 collisions of activated molecules. W. J. Jones and H. G. Williams[9] have examined the action of chlorine on isoprene and have obtained a 38% yield of α-chloro-β-methylbutadiene, purified through the sulphone compound. A higher-boiling dichloride, αδ-dichloro-β-methyl-Δ^{β}-butene, was also obtained in 45% yield.

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[97] *Ber.*, 1934, **67**, [*B*], 92, 1159, 1164; *A.*, 283, 879.
[98] *Compt. rend.*, 1934, **199**, 367; *A.*, 990.
[99] *Coll. Czech. Chem. Comm.*, 1934, **6**, 162; *A.*, 852.
[1] *Z. physikal. Chem.*, 1933, [*B*], **23**, 358; *A.*, 1934, 168.
[2] *Sintet. Kauchuk*, 1933, No. 1, 4; *A.*, 1934, 55.
[3] H. B. Dykstra, *J. Amer. Chem. Soc.*, 1934, **56**, 1625; *A.*, 990.
[4] *Ibid.*, 1933, **55**, 4665; *A.*, 1934, 55.
[5] *Ibid.*, 1934, **56**, 1169; *A.*, 754.
[6] *Ibid.*, p. 1167; *A.*, 753.
[7] *Sintet. Kauchuk*, 1933, No. 4, 11; *A.*, 1934, 1089.
[8] *J. Amer. Chem. Soc.*, 1933, **55**, 4109; *A.*, 1933, 1249.

H. I. Watermann and A. J. Tulleners have polymerised *iso*butene in heptane solution in the presence of aluminium chloride to give mixtures of olefinic and cyclic products (*M* 132—480).[10] S. F. Lebedev and I. A. Livschitz[11] have examined the depolymerisation of tri*iso*butene, $(C_4H_8)_3$, in the presence of floridin (active silicate) and have obtained a dimeride and a monomeride.

The polymerisation of unsaturated hydrocarbons by alkali metals and alkali metal alkyls has been investigated by K. Ziegler and his collaborators.[12] Lithium is soluble in ethereal solutions of butadiene (I), $\Delta^{\alpha\gamma}$-pentadiene (II), and βγ-dimethylbutadiene (III) and isoprene to give with (I) a resin of high molecular weight, with (II) pentene and $H(C_5H_8)_nH$ ($n = 2$—5). An intermediate lithium compound is formed, $CH_2Li{\cdot}C(CH_3){:}C(CH_3){\cdot}CH_2Li$, which reacts rapidly with a second molecule of (III). R. S. M.

Carbohydrates.

General.—The report comes to hand of the preparation of β-*l*-allose and β-*l*-altrose from *l*-ribose by the cyanohydrin synthesis:[13] preparations which complete the list of the sixteen theoretically possible aldohexoses and set a seal to the great work of Emil Fischer. β-*d*-Allose and α-galaheptose, hitherto known only as syrups, have now been obtained in crystalline form;[14] improved methods for the preparation of *d*-arabinose[15] and *l*-sorbose and of various acyl derivatives of the latter are described,[16] and the naturally occurring sedoheptose is recognised as *d*-altroketoheptose.[17]

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[9] *J.*, 1934, 829; *A.*, 864.

[10] *Rec. trav. chim.*, 1934, **53**, 699; *A.*, 864.

[11] *J. Gen. Chem. Russ.*, 1934, **4**, 13; *A.*, 864.

[12] K. Ziegler, F. Dersch, and H. Wollthan; K. Ziegler, L. Jacob, H. Wollthan, and A. Wenz, *Annalen*, 1934, **511**, 13, 45, 64; *A.*, 865.

[13] W. C. Austin and F. L. Humoller, *J. Amer. Chem. Soc.*, 1934, **56**, 1153; *A.*, 759.

[14] F. P. Phelps and F. Bates, *ibid.*, p. 1250; *A.*, 759; R. M. Hann, A. T. Merrill, and C. S. Hudson, *ibid.*, p. 1644; *A.*, 992.

[15] R. C. Hockett and C. S. Hudson, *ibid.*, p. 1632; *A.*, 992.

[16] H. H. Schlubach and J. Vorwerk, *Ber.*, 1933, **66**, [*B*], 1251; *A.*, 1933, 1146; K. Maurer and B. Schiedt, *Biochem. Z.*, 1934, **271**, 61; *A.*, 928; G. Arragon, *Compt. rend.*, 1934, **198**, 1508; *A.*, 760.

[17] V. Ettel, *Coll. Czech. Chem. Comm.*, 1933, **4**, 502, 513; *A.*, 1933, 47, 54.

Exigencies of space make it impossible to refer to all of the many new preparations of sugar derivatives, but attention should be directed to the remarkable use made of the amine,

$$NH_2{\cdot}CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}OH$$

(obtained by the reduction of *l*-arabinose oxime), in R. Kuhn's noteworthy synthesis of a lactoflavin [18] which has physiological properties identifying it with vitamin B_2. Also worthy of attention are derivatives of fructose such as the crystalline 1 : 3 : 4 : 6-tetrabenzoyl fructose,[19] the 2 : 3-*iso*propylidene-α-*d*-fructofuranose,[20] and a crystalline γ-methylfructoside,[21] all of which may have valuable synthetic uses.

A synthesis of cellobiose is reported.[22] Acetobromoglucose and lævoglucosan are condensed in the presence of silver carbonate and preferential opening of the 1 : 6-oxide ring is effected by means of 50% sulphuric acid. Acetylation of the product yields cellobiose octa-acetate, from which the free sugar is obtained by the usual methods. Improvements in technique have led to the isolation in crystalline form of *iso*trehalose (ββ-trehalose) [23] and of 6-β-*d*-galactosido-*d*-glucose.[24] The latter dissaccharide is probably identical with the allolactose isolated from human milk.[25]

Stachyose, found in the tubers of *Stachys tubifera*, in ash manna, and in other plants, is a non-reducing tetrasaccharide which, on hydrolysis with dilute acetic acid, gives fructose and the reducing trisaccharide, manninotriose; the latter is composed of galactose (2 mols.) and glucose (1 mol.). A careful study [26] of the hydrolytic products of fully methylated stachyose and manninotrionic acid shows that in stachyose the fructofuranose and glucopyranose residues are united through their reducing groups; that the reducing group of one galactopyranose residue is linked to C4 of the glucose, and the sixth carbon atom of the former is combined with the reducing group of the second galactopyranose residue. The form of linkage (α or β) between the individual monoses remains a matter for conjecture, although useful suggestions have been made, on general grounds, by E. F. Armstrong and K. F. Armstrong.[27]

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[18] R. Kuhn and F. Weygand, *Ber.*, 1934, **67**, [*B*], 1932, 1936, 2084.

[19] P. Brigl and R. Schinle, *ibid.*, p. 127; *A.*, 281.

[20] L. Zervas and P. Sessler, *ibid.*, 1933, **66**, 1698; *A.*, 1934, 58.

[21] C. B. Purves and C. S. Hudson, *J. Amer. Chem. Soc.*, 1934, **56**, 708; *A.*, 513.

[22] K. Freudenberg and W. Nagai, *Ber.*, 1933, **66**, [*B*], 27; *A.*, 1934, 48.

[23] H. H. Schlubach and W. Schetelig, *Z. physiol. Chem.*, 1932, **213**, 83; *A.*, 1933, 148.

[24] B. Helferich and G. Sparmberg, *Ber.*, 1933, **66**, [*B*], 806; *A.*, 1934, 699.

[25] M. Polonowski and A. Lespagnol, *Compt. rend.*, 1932, **195**, 465; *A.*, 1932, 1021.

[26] M. Onuki, *Proc. Imp. Acad. Tokyo*, 1932, **8**, 496; *A.*, 1933, 378.

Monomethyl Derivatives of Monosaccharides.—The four possible monomethyl glucopyranoses are now known and their structures have been allocated with some degree of certainty. Since, however, some confusion has existed in this group, it is desirable to indicate the evidence upon which the present views are based. H. Ohle and L. von Vargha [28] prepared a monomethyl glucose by the action of sodium methoxide on 5 : 6-anhydro-1 : 2-monoacetone glucose, followed by the removal of the acetone residue, the methylation occurring by the opening of the 5 : 6-anhydro-ring. The product was therefore either 5- or 6-methyl glucose (the possibility of a Walden inversion having occurred at position 5 was envisaged, but idose derivatives were not formed). The monomethyl glucose was a crystalline solid, m. p. 143°, forming an osazone, m. p. 180°. In these properties and in its specific rotation it appeared to be different from the 6-monomethyl glucose prepared by B. Helferich and J. Becker,[29] which was a syrup. It was therefore presumed to be 5-methyl glucose. If this were its constitution, it followed that it must belong to the furanose series and should give rise only to a furanoside with methyl-alcoholic hydrogen chloride. P. A. Levene and A. L. Raymond,[30] however, find that both a methylfuranoside and a methylpyranoside are produced under these conditions, and, rejecting the possibility of the migration of a methyl group, regard the sugar as 6-methyl glucose identical with that of Helferich and Becker. Helferich [31] later corrected the constants of his 6-methyl glucose, and although the latter substance could not be induced to crystallise, its properties agreed closely with those of Ohle's substance. Further evidence cited by Levene and Raymond shows clearly that Ohle's substance is 6-methyl glucose.

In 1924 E. Pacsu [32] prepared a mono- and a supposed tri-methyl glucose from an acetone derivative of glucose mercaptal and concluded that the methyl group was at position 4 in the monomethyl derivative, on the grounds that it showed different properties from those of the known 2-, 3-, and 6-methyl sugars. Later investigation of this compound by Levene [33] and by R. Schinle [34] revealed that the supposed monomethyl glucosazone prepared from it was really glucosazone; the elimination of the methyl group during the process suggests that the compound was really 2-methyl glucose, a conclusion that is supported by its giving a methyl saccharic acid on oxidation with nitric acid, by its difference from the well-characterised 3-methyl glucose, and by the exclusion of positions 4 and 5 by the changes in rotation which occur during glucoside formation. This crystalline monomethyl glucose (m. p. 156—157°) is therefore 2-methyl glucose, identical with that prepared by W. J. Hickinbottom[35] and by P. Brigl and R. Schinle.[36] Meanwhile Schinle[34] had proved that two monomethyl glucoses are produced by Pacsu's method, the second being a substance which Pacsu wrongly described as 4 : 5 : 6-trimethyl glucose. This new monomethyl glucose was a syrup which gave an osazone, m. p. 160°, the specific rotation of which, and that of the original sugar, differentiated the latter from the known 2-, 3-, and 6-methyl glucoses as well as from the Ohle and Vargha compound, which at that time (1932) was regarded as 5-methyl glucose. Schinle therefore assigned the position 4 to the methyl group in the new compound, although now, since the so-called 5-methyl glucose is identified as 6-methyl glucose, Schinle's compound may be either 4-methyl or 5-methyl glucose. Levene and Raymond[37] then prepared a monomethyl triacetyl methylglucoside by the following route: 4 : 6-benzylidene β-methylglucoside gave, on benzoylation and selective hydrolysis, 2 : 3-dibenzoyl β-methylglucoside, which by partial benzoylation gave 2 : 3 : 6-tribenzoyl β-methylglucoside (that the benzoyl group had entered position 6 and not position 4 was shown by the non-identity of the acetyl derivative with the known 6-acetyl 2 : 3 : 4-tribenzoyl methylglucoside). If it be assumed that neither ring nor group interchange has occurred during these processes, it follows that the only free hydroxyl is at position 4. Methylation, debenzoylation with barium oxide in methyl alcohol, followed by acetylation, yielded 4-methyl-2 : 3 : 6-triacetyl β-methylglucoside, and this was found to be identical with a derivative prepared through the aceto-bromo-compound from Schinle's monomethyl glucose, which would appear to be, therefore, 4-methyl glucose.

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[27] *Chem. and Ind.*, 1934, **53**, 912; *A.*, 1338.

[28] *Ber.*, 1929, **62**, 2435; *A.*, 1929, 1279.

[29] *Annalen*, 1924, **440**, 13; *A.*, 1925, i, 9.

[30] *J. Biol. Chem.*, 1932, **97**, 751; *A.*, 1932, 1115.

[31] B. Helferich and E. Günther, *Ber.*, 1931, **64**, [*B*], 1276; *A.*, 1931, 939.

[32] *Ber.*, 1924, **57**, 849; 1925, **58**, 1455; *A.*, 1924, i, 712; 1925, i, 1242.

[33] P. A. Levene, G. M. Meyer, and A. L. Raymond, *J. Biol. Chem.*, 1931, **91**, 497; *A.*, 1931, 825.

[34] *Ber.*, 1932, **65**, [*B*], 315; *A.*, 1932, 369.

Open-chain Sugars.—The structure of monosaccharides is not limited, on theoretical grounds, to ring systems containing either six atoms (pyranoses) or five atoms (furanoses), but until recently structures other than the stable pyran ring or the more labile furan ring had not been characterised. Postulations of open-chain structures (free aldehyde or free ketone) have been freely made in the past to explain the mechanism of mutarotation and particularly to satisfy the requirements of the enolisation involved in the action of alkali on sugars. The existence of such acyclic tautomerides of the sugars is now an established fact and, resulting from the study of such open-chain derivatives, comes the report of a third type of ring structure containing seven atoms, several representatives of which in the hexoses have now been prepared. The term septanose has been applied to these seven-membered ring forms.[38]

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[35] *J.*, 1928, 3140; *A.*, 1929, 174.

[36] *Ber.*, 1930, **63**, 2884; *A.*, 1931, 71.

[37] *J. Biol. Chem.*, 1932, **97**, 763; *A.*, 1933, 54.

Two chief methods are now available for the preparation of derivatives of open-chain monosaccharides; they take advantage of the fission of the pyranose ring which appears to occur when sugars are condensed with ethyl mercaptan or hydroxylamine. P. A. Levene and G. M. Meyer in 1926 prepared 2 : 3 : 4 : 5 : 6-pentamethyl derivatives of glucose, mannose, and galactose by methylation of the corresponding di-ethylmercaptal, followed by hydrolysis of the mercaptal group. Better characterised, however, are the crystalline acyl derivatives, the acetates[39] and the benzoates.[40] M. L. Wolfrom and his co-workers,[41] having prepared a number of crystalline open-chain aldoses by the hydrolysis of acetylated thioacetals, now report the synthesis of a *keto*-fructose penta-acetate by the application of the same method to fructose di-ethylmercaptal. The method of preparation of this *keto*-fructose penta-acetate leaves no doubt as to its open-chain structure and it is found to be identical with the so-called α-fructose penta-acetate of C. S. Hudson and D. H. Brauns, which is prepared, together with the true β-fructose penta-acetate, by the acetylation of β-fructose tetra-acetate. Such an open-chain structure had already been assigned to " α "-fructose penta-acetate by E. Pacsu and F. V. Rich,[42] since on catalytic reduction and subsequent acetylation it gives a mixture of hexa-acetyl *d*-mannitol and hexa-acetyl *d*-sorbitol. By similar methods the latter authors have shown that the " third " turanose octa-acetate is a derivative of open-chain fructose.

An open-chain methyl pentose, namely, *aldehydo-l*-fucose tetra-acetate, has been prepared.[43] This compound has the unusual low solubility in all solvents shown by *aldehydo*-galactose tetra-acetate[44] and, like *aldehydo*-galactose penta-acetate, differs from the other *aldehydo*-acetates in forming well-defined carbonyl addition compounds. By condensing β-galactopyranose tetra-acetate and β-galactofuranose tetra-acetate with methylphenylhydrazine, J. Compton and M. L. Wolfrom[45] show that the same hydrazone is produced from each and that it is identical after acetylation with that formed from *aldehydo*-galactose penta-acetate, indicating that hydrazone formation involves opening of the lactal ring, the furanose lactal opening forty-five times as rapidly as the pyranose at 0°.

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[38] F. Micheel and F. Suckfüll, *Annalen*, 1933, **502**, 85; *A.*, 1933, 594.

[39] M. L. Wolfrom, *J. Amer. Chem. Soc.*, 1929, **51**, 2188; *A.*, 1929, 1043.

[40] P. Brigl and H. Mühlschlegel, *Ber.*, 1930, **63**, 1551; *A.*, 1930, 1022.

[41] *J. Amer. Chem. Soc.*, 1930, **52**, 2464, 3619; *A.*, 1930, 1023, 1411; *ibid.*, 1931, **53**, 4379; *A.*, 1931, 1039; *ibid.*, 1934, **56**, 985; *A.*, 760.

[42] *Ibid.*, 1933, **55**, 3018; *A.*, 1933, 937.

[43] M. L. Wolfrom and J. A. Orsino, *ibid.*, 1934, **56**, 985; *A.*, 636.

[44] M. L. Wolfrom, *ibid.*, 1931, **53**, 2275; *A.*, 1931, 1039; M. L. Wolfrom and W. M. Morgan, *ibid.*, 1932, **54**, 3390; *A.*, 1932, 1021.

The α-*d*-glucoheptulose prepared by the action of dilute alkali on α-*d*-glucoheptose[46] shows no mutarotation and therefore might possibly be an acyclic sugar. Acetylation with acetic anhydride and sodium acetate gives a dextrorotatory hexa-acetate, a fact that at first sight lent some support to the view that the hexa-acetate might have an open-chain structure. A method has, however, been developed[47, 48] for distinguishing between open-chain and cyclic sugar acetates. This consists in treating the acetate (or benzoate) with ethyl mercaptan in the presence of zinc chloride : the open-chain " α "-fructose penta-acetate so treated yields a mercaptal containing the same number of acetyl groups as the original acetate, whereas the cyclic β-fructose penta-acetate gives β-thioethyl fructose tetra-acetate. This method was similarly used to prove the open-chain structure of a new crystalline fructose pentabenzoate.[49] The application of this reaction to *d*-glucoheptulose hexa-acetate resulted in the replacement of two acetate groups by ethylmercapto-groups, indicating that the hexa-acetate was not an open-chain compound.[50]

Acetylation of sugar oximes is complicated by the fact that nitriles may be produced as well as the acetylated oxime. Thus, Deulofeu and Wolfrom and their co-workers[51] have shown that the low-temperature acetylation of galactose oxime leads to a mixture of three products, namely, galactononitrile penta-acetate, *aldehydo*-galactose oxime hexa-acetate, and an isomeride of the latter. The open-chain galactose oxime hexa-acetate (I) is hydrolysed[52] by oxalic acid to the penta-acetate (II), and the latter on treatment with nitrous acid gives *aldehydo*-*d*-galactose penta-acetate (III).

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[45] *J. Amer. Chem. Soc.*, 1934, **56**, 1157; *A.*, 760.

[46] W. C. Austin, *ibid.*, 1930, **52**, 2106; *A.*, 1930, 894.

[47] M. L. Wolfrom and A. Thompson, *ibid.*, 1934, **56**, 880; *A.*, 636.

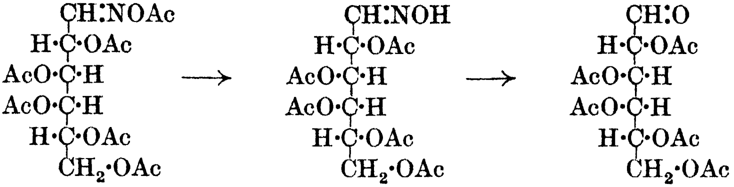
[48] P. Brigl, H. Mühlschlegel, and R. Schinle, *Ber.*, 1931, **64**, 2932; *A.*, 1932, 147.

[49] *Ibid.*, 1933, **66**, [*B*], 325; *A.*, 1933, 148.

[50] M. L. Wolfrom and A. Thompson, *J. Amer. Chem. Soc.*, 1934, **56**, 1804; *A.*, 1092.

[51] *Ibid.*, 1933, **55**, 3488; *A.*, 1933, 1038.

[52] M. L. Wolfrom, L. W. Georges, and S. Soltzberg, *ibid.*, 1934, **56**, 1794; *A.*, 1092.

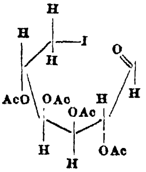


$$\begin{array}{c}\mathrm{CH{:}NOAc}\\ \mathrm{H{\cdot}C{\cdot}OAc}\\ \mathrm{AcO{\cdot}C{\cdot}H}\\ \mathrm{AcO{\cdot}C{\cdot}H}\\ \mathrm{H{\cdot}C{\cdot}OAc}\\ \mathrm{CH_2{\cdot}OAc}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH{:}NOH}\\ \mathrm{H{\cdot}C{\cdot}OAc}\\ \mathrm{AcO{\cdot}C{\cdot}H}\\ \mathrm{AcO{\cdot}C{\cdot}H}\\ \mathrm{H{\cdot}C{\cdot}OAc}\\ \mathrm{CH_2{\cdot}OAc}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH{:}O}\\ \mathrm{H{\cdot}C{\cdot}OAc}\\ \mathrm{AcO{\cdot}C{\cdot}H}\\ \mathrm{AcO{\cdot}C{\cdot}H}\\ \mathrm{H{\cdot}C{\cdot}OAc}\\ \mathrm{CH_2{\cdot}OAc}\end{array}$$

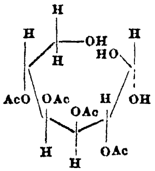
(I.) (II.) (III.)

The *aldehydo*-galactose penta-acetate is easily separable from the galactonitrile penta-acetate. A method is thus provided of synthesising the open-chain acetates of those disaccharides and ketoses whose thioacetals are not available. The semicarbazones may be used in exactly the same way as the oximes.

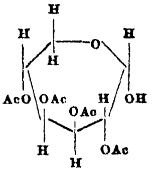
The Septanoses.—Micheel and Suckfüll[38] prepared 6-iodo-*d*-galactose mercaptal 2 : 3 : 4 : 5-tetra-acetate from 6-iodo-diacetone-galactose by hydrolysis of the acetone groups, followed by treatment with ethyl mercaptan and acetylation of the product. This thioacetal on hydrolysis by Wolfrom's method with mercuric chloride and cadmium carbonate in the cold yields the open-chain 6-iodo-tetra-acetyl *aldehydo*-galactose (IV). If, however, during the treatment with mercuric chloride the temperature is allowed to rise to 40°, a further reaction takes place, involving the removal of the iodine and the formation of the open-chain hydrate (V). Non-reversible ring closure occurs in pyridine solution, yielding the seven-membered cyclic sugar, 2 : 3 : 4 : 5-tetra-acetyl *d*-galactoseptanose (VI). Acetylation of (VI) yields a separable mixture of crystalline α- and β-1 : 2 : 3 : 4 : 5-penta-acetyl *d*-galactoseptanoses. In the hydrolysis with mercuric chloride, the chief product of the reaction is not the hydrate (V), but the normal tetra-acetyl galactopyranose produced as the result of acyl migration.



(IV.)



(V.)



(VI.)

The seven-membered ring structure is confirmed[53] by the preparation, by standard methods, of tetramethyl methylgalactoseptanoside from the α- and β-galacto-septanose penta-acetates. That the methyl groups in this derivative are substituted in positions

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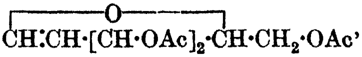
[53] F. Micheel and F. Suckfüll, *Annalen*, 1933, **507**, 138; *A.*, 1933, 1278.

2, 3, 4, and 5 is shown by its oxidation with nitric acid to tetramethyl mucic acid. The stability of the septanose ring seems to be of the order of that of the furanose ring.[54] The rate of hydrolysis of α-methylgalactoseptanoside is of the same order as that of the furanosides and, although the ready hydrolysis cannot be ascribed to ring strain (the seven-membered ring is practically strainless), the septanose ring is definitely much less stable than the pyranose ring. Hydrolysis, for instance, of either penta-acetate of galactoseptanose with weak alkali yields pure galactopyranose. Nevertheless, it is conceivable that under certain conditions an equilibrium mixture containing the septanose may exist, as, for example, in the preparation of methylfuranosides with cold methyl-alcoholic hydrogen chloride. A careful examination of the products in this case might reveal the presence of methylseptanosides.

Action of Pyridine.—S. Danilow and his co-workers [55] observed that glucose was converted into fructose by heating in anhydrous pyridine or quinoline. This reaction has been further studied and is interesting on theoretical grounds, though the yields obtainable are too small to render the method available for the preparation of ketoses from aldoses. It has been suggested [56] that the transformation is conditioned by the spatial arrangement with respect to each other of the OH groups on the second and third carbon atoms, for the *cis*-2 : 3-aldoses appear to yield a larger proportion of ketose than do the *trans*-2 : 3-aldoses. However, there seems to be no rigid line of demarcation between the two types. For instance, mannose is converted to the extent of 30%, whereas only 11% of glucose is transformed into fructose; but, on the other hand, *l*-rhamnose (*cis*-2 : 3) gives only 16% of the corresponding ketose, and *d*-xylose (*trans*-2 : 3) is converted to an equal extent. The *d*-xyloketose [57] produced from the latter appears to be the optical enantiomorph of the sugar isolated some years ago from the urine of a case of pentosuria.[58] *d*-Galactose (also *trans*-2 : 3) is converted into *d*-tagatose in fair yield.[59]

The Glucals.—Further study of this group of unsaturated sugar derivatives exemplifies their extraordinary reactivity and the ease with which, under the mildest conditions, they undergo transformation. Triacetyl glucal,  $\mathrm{CH{:}CH{\cdot}[CH{\cdot}OAc]_2{\cdot}CH{\cdot}CH_2{\cdot}OAc}$, by boiling with water yields diacetyl ψ-glucal,

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[54] F. Micheel and F. Suckfüll, *Ber.*, 1933, **66**, [*B*], 1957; *A.*, 1934, 174.

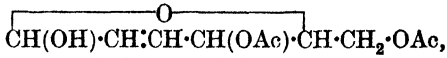
[55] *Ibid.*, 1930, **63**, 2269; *A.*, 1930, 1411.

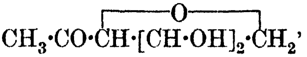
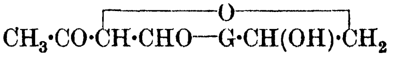
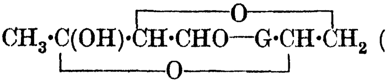
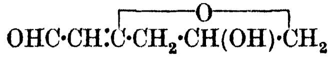
[56] P. A. Levene and D. W. Hill, *J. Biol. Chem.*, 1933, **102**, 563; *A.*, 1933, 1278.

[57] O. T. Schmidt and R. Treiber, *Ber.*, 1933, **66**, [*B*], 1765; *A.*, 1934, 173.

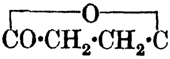
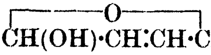
[58] P. A. Levene and F. B. La Forge, *J. Biol. Chem.*, 1914, **18**, 319.

[59] T. Reichstein and W. Bosshard, *Helv. Chim. Acta*, 1934, **17**, 753; *A.*, 872.

 $\mathrm{CH(OH){\cdot}CH{:}CH{\cdot}CH(OAc){\cdot}CH{\cdot}CH_2{\cdot}OAc}$,

and the latter, on hydrolysis with barium hydroxide, gives, not ψ-glucal itself, but an isomeride, *iso*glucal, to which the structure,  $\mathrm{CH_3{\cdot}CO{\cdot}CH{\cdot}[CH{\cdot}OH]_2{\cdot}CH_2}$, is assigned [60] and which is characterised by its crystalline benzylphenylhydrazone. This structure has been allocated to *iso*glucal by analogy with *iso*lactal, which has been chosen for structural investigation in preference to *iso*glucal because of the greater instability of the latter. *iso*Lactal is prepared from hexa-acetyl lactal through the intermediate acetyl ψ-lactal and is therefore 4-galactosido*iso*glucal; it is resolved into its two components by kefir extract. Bergmann considers *iso*lactal to be a mixture of dynamic isomerides,  $\mathrm{CH_3{\cdot}CO{\cdot}CH{\cdot}CHO{-}G{\cdot}CH(OH){\cdot}CH_2}$ $\rightleftharpoons$  $\mathrm{CH_3{\cdot}C(OH){\cdot}CH{\cdot}CHO{-}G{\cdot}CH{\cdot}CH_2}$ (G = galactose residue). Hydrolysis of acetyl ψ-lactal by barium hydroxide yields only *iso*lactal, but in the similar hydrolysis of acetyl ψ-glucal there is obtained, together with *iso*glucal, a substance which contains one molecule of water less than *iso*glucal. It possesses the properties of E. Fischer's original " glucal " and for that reason has been named protoglucal. Its properties suggest the presence in it of an aldehyde group and its structure most probably is  $\mathrm{OHC{\cdot}CH{:}C{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2}$, which explains why ψ-lactal does not give a protolactal, the fourth carbon atom being " protected " by the galactose residue.

The so-called penta-acetyl and hexa-acetyl maltal hydrates of M. Bergmann and G. Kobel [61] are shown to be hepta-acetyl and octa-acetyl maltose respectively by W. N. Haworth, E. L. Hirst, and R. J. W. Reynolds,[62] who have prepared the true hexa-acetyl maltal. Oxidation of maltal with perbenzoic acid gives 4-α-glucosido-β-mannose, the epimeride of maltose.

Following the discovery of P. A. Levene and T. Mori [63] that the pentodesoses are converted into lævulic acid by strong mineral acids, M. Bergmann and H. Machemer [64] find that methyl-alcoholic hydrogen chloride converts glucal and ψ-glucal triacetates into methyl δ-methoxymethyl lævulate. The formation of lævulic acid,  $\overbrace{\mathrm{CO{\cdot}CH_2{\cdot}CH_2{\cdot}C}}^{\mathrm{O}}\mathrm{(OH){\cdot}CH_3}$, from a ψ-pental,  $\overbrace{\mathrm{CH(OH){\cdot}CH{:}CH{\cdot}CH}}^{\mathrm{O}}\mathrm{{\cdot}CH_2{\cdot}OH}$, involves the shifting of the double bond along the carbon chain towards the primary group, a change that may be effected by the alternate addition and removal of a molecule of water.

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[60] M. Bergmann, L. Zervas, and J. Engler, *Annalen*, 1933, **508**, 25; *A.*, 1934, 173.

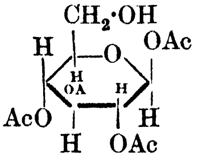
[61] *Ibid.*, 1923, **434**, 109; *A.*, 1924, i, 265.

[62] *J.*, 1934, 302; *A.*, 513.

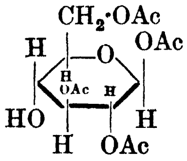
[63] *J. Biol. Chem.*, 1929, **83**, 803; *A.*, 1929, 1277.

[64] *Ber.*, 1933, **66**, [*B*], 1063; *A.*, 1933, 937.

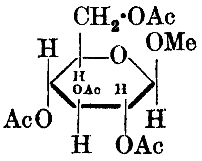
Acyl Migration.—The multiplying instances of the ease with which, in the sugar series, acyl groups may, under the influence of weak alkali, become detached from one carbon atom and become associated with a second, points to the need for caution in ascribing structures to acylated sugars and limits their utility as synthetic agents.[66] Helferich [65] observed what appeared to be mutarotation in a solution of 1 : 2 : 3 : 4-tetra-acetyl β-*d*-glucose (I), but investigation showed that the rotational changes were due to the migration of an acetyl group from C_4 to C_6 (under the influence of the minute amount of alkali coming from the soft glass of the polarimetric tube) and a new product, 1 : 2 : 3 : 6-tetra-acetyl β-*d*-glucose (II), was isolated in crystalline form. Treatment of the latter substance with the Purdie reagents led to an unexpected result; a methyl group entered, not at position 4, but at position 1 and the product was 2 : 3 : 4 : 6-tetra-acetyl β-methylglucoside (III). Apparently a second migration of an acetyl group had occurred, from position 1 to position 4, presumably induced by the weak alkalinity of the methylating agents.



(I.)

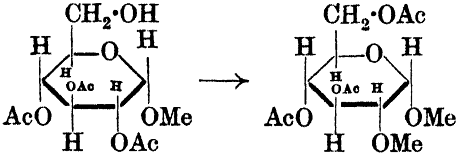


(II.)



(III.)

Acyl migration from position 2 to position 6 is observed when 2 : 3 : 4-triacetyl α-methylglucoside (IV) is methylated [66] with the same reagents, the product being 3 : 4 : 6-triacetyl 2-methyl α-methylglucoside (V).

(IV.)  (V.)

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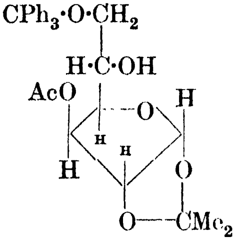
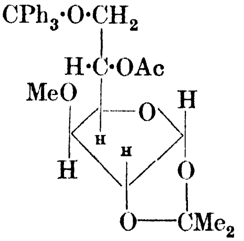
[65] B. Helferich and W. Klein, *Annalen*, 1926, **450**, 219; 1927, **455**, 173; *A.*, 1927, 135, 858.

[66] W. N. Haworth, E. L. Hirst, and E. G. Teece, *J.*, 1931, 2858; *A.*, 1932, 45.

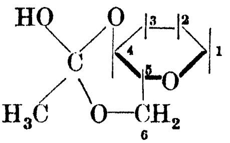
Acyl migration from C_4 to C_6 also occurs when 4-acetyl-2 : 3-dimethyl α-methylglucoside is methylated,[67] for the expected 2 : 3 : 6-trimethyl glucose (after hydrolysis) was accompanied by 2 : 3 : 4-trimethyl glucose (characterised as the crystalline 1 : 6-dinitrate). Acyl migration from C_3 to C_5 is described by L. von Vargha,[68] 3-acetyl-6-triphenylmethyl monoacetone glucose (VI), on methylation, giving 5-acetyl-3-methyl-6-triphenylmethyl monoacetone glucose (VII).



(VI.)



(VII.)



(VIII.)

That the methyl group enters at position 3 and not at position 5 is shown by the preparation of the same compound (VII) from the 3-methyl-monoacetone glucose of K. Freudenberg, W. Dürr, and H. v. Hochstetter.[69] A migration of an acetyl group from position 3 to position 6 in monoacetone glucose had already been observed [70] and a wandering from C_5 to C_6 during ring closure is reported [38] in the case of 2 : 3 : 4 : 5-tetra-acetyl 6-iodo-galactose mercaptal. The chief product of the action of mercuric chloride on this compound at 40° is 2 : 3 : 4 : 6-tetra-acetyl galactopyranose (see under " septanoses ").

The transfer of an acetyl group from one carbon atom to another finds its most feasible explanation in the formation of an ortho-acetic acid derivative as intermediate, a mechanism first suggested by Fischer. Considerations of strain would seem, at first sight, to preclude the formation of a ring system involving the *trans*-situated linkages of, say, C_4 and C_6 in (I). Reference to models, however, shows that such a six-membered ring would, in fact, be strainless and that there is, on stereochemical grounds at least, nothing to prevent a direct transfer of an acetyl group from C_4 to C_6, by the intermediate formation of the orthoacetic ester (VIII).[65]

Anhydro-sugars.—It is now well known that the introduction of the *p*-toluenesulphonyl group into the sugar molecule more profoundly affects the properties of the latter than does the introduction of either the acetyl or the benzoyl group; in fact the toluenesulphonyl group more closely resembles the halogens in this respect. Like the latter, its cautious removal by means of alkali leads to the formation of a subsidiary oxygen-bridge between the carbon to which the group was attached and a second carbon having a free hydroxyl group. A general view of the reaction is not yet available, but various anhydro-sugars have been described, their constitutions in many cases not being known with certainty. Among the better authenticated examples of anhydro-sugars prepared by removal of *p*-toluenesulphonyl residues are 1 : 2-monoacetone 3 : 6-anhydro-α-*d*-glucofuranose (I),[71] a derivative of the anhydro-sugar of E. Fischer and K. Zach; 3 : 6-anhydro-α-methyl-*d*-galactopyranoside (II);[72]

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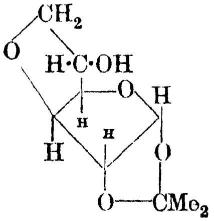
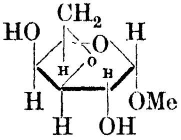
[67] G. J. Robertson, *J.*, 1933, 737; *A.*, 1933, 937.

[68] *Ber.*, 1934, **67**, [*B*], 1223; *A.*, 872.

[69] *Ibid.*, 1928, **61**, 1740; *A.*, 1928, 1222.

[70] K. Josephson, *Annalen*, 1929, **472**, 217; *A.*, 1929, 912.


(I.)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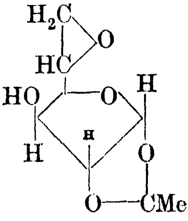
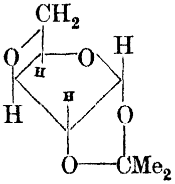
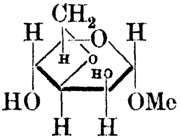

(III.)

5 : 6-anhydro-1 : 2-monoacetone *d*-glucofuranose (III);[28] and 3 : 5-anhydro-1 : 2-monoacetone *d*-xylose (IV).[73] In each of these cases,


(IV.)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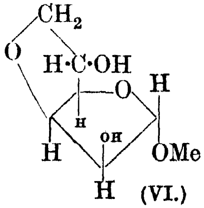
(VI.)

the *p*-toluenesulphonyl group was originally attached to the carbon of the primary alcohol group. (II) has also been prepared from α-methylgalactoside 6-bromohydrin,[74] and the corresponding 3 : 6-anhydro-α-methylmannopyranoside (V) from α-methylmannoside-6-bromohydrin.[75] Hydrolysis of (V) yields a 3 : 6-anhydromannose which forms an osazone identical with that from 3 : 6-anhydroglucose. The anhydromannose is converted by methyl-alcoholic hydrogen chloride into 3 : 6-anhydro-α-methylmannofuranoside (VI) different from (V).

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[71] H. Ohle, L. von Vargha, and H. Erlbach, *Ber.*, 1928, **61**, 1211; *A.*, 1928, 871.

[72] H. Ohle and H. Thiel, *Ber.*, 1933, **66**, [*B*], 525; *A.*, 1933, 492.

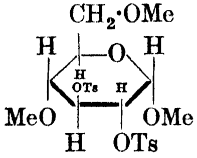
[73] P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, 1933, **102**, 315; *A.*, 1933, 1144.

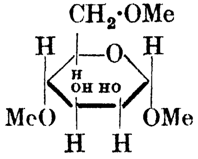
[74] F. Valentin, *Coll. Czech. Chem. Comm.*, 1932, **4**, 364; *A.*, 1932, 1237.

[75] *Idem*, *ibid.*, 1934, **6**, 354; *A.*, 1206.

When the toluenesulphonyl group is attached, not to the primary alcoholic group, but to some other in the chain, anhydro-ring formation on its removal may be accompanied by Walden inversion on one or other of the carbon atoms or on both, a phenomenon which is not confined to the sugar group (see, for instance, the work of Kenyon and his collaborators).[76] The alkaline hydrolysis of 2 : 3-di-*p*-toluenesulphonyl-4 : 6-dimethyl α-methylglucopyranoside (VII) yields a dimethyl methylhexoside (26%) and a crystalline dimethyl anhydromethylhexoside (66%), neither of which appears to be a derivative of glucose.[77]

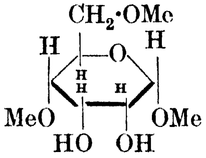
(VII.)

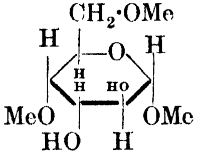




(VIII.)

(IX.)





(X.)

There are several possibilities to envisage. The formation of the 2 : 3-ethylene oxide bridge and its subsequent fission may be accompanied by (i) inversion at C_2, whereby mannose derivatives will result (VIII); (ii) inversion at C_3, giving allose derivatives (IX); or (iii) inversion at both C_2 and C_3, whereby an altrose derivative (X) will be formed. A lack of knowledge of the derivatives of these rarer sugars precludes at present a final decision being made and little more can be said than that Walden inversion seems undoubtedly to have occurred. Similar evidence of inversion is given by W. N. Haworth, E. L. Hirst, and L. Panizzon,[78] who isolate a crystalline dimethyl derivative of anhydro-β-methylhexoside (prepared by the graded hydrolysis of 2-*p*-toluenesulphonyl 3 : 4 : 6-triacetyl β-methylglucopyranoside), which they are inclined to regard as a mannose derivative; the high negative rotation of the hydrolysis product of the unmethylated anhydromethylhexoside suggests that a further inversion occurs and the substance passes into the altrose series (cf. VIII and X). Similar indications of Walden inversion appear in the preparation of an anhydrohexoside by the deacylation of 4-*p*-toluenesulphonyl 2 : 3 : 6-diacetyl β-methylglucopyranoside,[80] and in the conversion of 2-*p*-toluenesulphonyl β-methylglucoside into methyl *epi*glucosamine.[79]

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[76] J. Kenyon, H. Phillips, and F. M. H. Taylor, *J.*, 1933, 173; *A.*, 1933, 604.

[77] D. S. Mathers and G. J. Robertson, *ibid.*, p. 1076; *A.*, 1933, 1037.

[78] *J.*, 1934, 154; *A.*, 394.

Ribose and the Nucleic Acids.—The biological importance of ribose has led to increased activity in the study of this hitherto rare sugar. Preparations of *l*-ribose from *l*-arabinal acetate,[81] of crystalline methyl-*d*-riboside from the free sugar,[82] of ribose-5-phosphoric acid, and of various acetone derivatives are described.[83] A study of the mutarotation of β-*d*-ribose and β-*l*-ribose by F. P. Phelps, H. S. Isbell, and W. Pigman [84] shows it to be unexpectedly complex; the mutarotation resembles that of the labile calcium chloride compound of mannose,[85] in which mannose very probably has a furanose structure.[86] On the basis of their reaction with triphenylmethyl chloride, H. Bredereck [87] allots a furanose structure to the ribose residues in the nucleosides uridine, cytidine, adenosine, and inosine. Although such conclusions, supported as they are by the isolation of 2 : 3 : 5-trimethyl ribofuranose from methylated guanosine,[88] are very possibly true, yet it should be observed that the assumption that triphenylmethyl chloride will react only with primary alcohol groups is no longer tenable. C. S. Hudson and R. C. Hockett [89] have prepared, in a crystalline state, a triphenylmethyl derivative of α-methyl-*l*-fucoside (which of course contains no primary alcohol group) and a bistriphenylmethyl β-methyl-*d*-xyloside. In the latter compound one of the triphenylmethyl radicals must have reacted with a secondary alcohol group. This demonstration invalidates all that type of evidence of structure which is based on the triphenylmethyl reaction, as, for instance, E. Pacsu's revised formulation of turanose and melezitose.[90]

Light has been thrown upon the mode of linkage of the carbohydrate and the purine in the naturally occurring purine nucleosides by a recent spectrographic method [91] which makes it possible to distinguish derivatives of xanthine substituted at position 7 from those where substitution occurs at position 9. It is shown, for instance, that in xanthinose from yeast nucleic acid the carbohydrate is probably attached at C_9, whilst the synthetic arabinoside and glucoside of theophylline contain the carbohydrate in position 7.

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[79] E. W. Bodycote, W. N. Haworth, and E. L. Hirst, *ibid.*, p. 151; *A.*, 396.

[80] B. Helferich and A. Müller, *Ber.*, 1930, **63**, 2142; *A.*, 1930, 1411; A. Müller, *ibid.*, 1934, **67**, [*B*], 421; *A.*, 513.

[81] W. C. Austin and F. L. Humoller, *J. Amer. Chem. Soc.*, 1934, **56**, 1152; *A.*, 759.

[82] J. Minsaas, *Annalen*, 1934, **512**, 286; *A.*, 1091.

[83] P. A. Levene and E. T. Stiller, *J. Biol. Chem.*, 1933, **102**, 187; 1934, **104**, 299; 1934, **106**, 421; *A.*, 1933, 1145; 1934, 390, 1091.

[84] *J. Amer. Chem. Soc.*, 1934, **56**, 747; *A.*, 494.

[85] J. K. Dale, *ibid.*, 1929, **51**, 2225; *A.*, 1929, 1280.

[86] H. S. Isbell, *ibid.*, 1933, **55**, 2166; *A.*, 1933, 699.

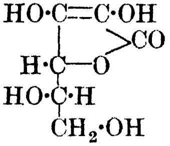
[87] *Ber.*, 1933, **66**, [*B*], 198; *A.*, 1933, 261; *Z. physiol. Chem.*, 1934, **223**, 61; *A.*, 394.

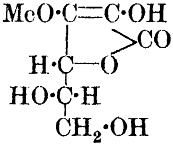
[88] P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, 1932, **97**, 491; *A.*, 1932, 1043.

[89] *J. Amer. Chem. Soc.*, 1934, **56**, 945, 947; *A.*, 635.

[90] *Ibid.*, 1931, **53**, 3099; *A.*, 1931, 1149.

Ascorbic Acid and its Analogues.—There has been much activity during the past year in the study of ascorbic acid and analogous substances. The formula (I) for *l*-ascorbic acid,[92] proof of which was given early in 1933, has now found universal acceptance and considerable progress has been made in the detailed investigation of substances containing this type of ring system.


(I.)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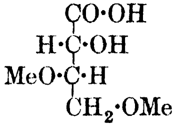

$$\begin{array}{l} \mathrm{CO{\cdot}OH} \\ \mathrm{H{\cdot}C{\cdot}OH} \\ \mathrm{MeO{\cdot}C{\cdot}H} \\ \mathrm{CH_2{\cdot}OMe} \end{array}$$

(III.)

It is a remarkable fact that ascorbic acid itself, with free hydroxyl groups in positions 2 and 3, does not undergo opening of the lactone ring in the presence of alkali. The 2 : 3-dimethyl derivative (IV) behaves normally, however, and under the influence of very dilute alkali solution gives the sodium salt of the open-chain acid (V). With the object of ascertaining which of the two enolic hydroxyl groups in ascorbic acid is the more acidic, studies have been made of the action of limited quantities of diazomethane on the acid. It now appears that under these conditions the main product is the 3-methyl ether [93] (II), the constitution of which follows from the observations that the new substance gives an intense blue coloration with aqueous ferric chloride and that on further methylation with diazomethane it yields crystalline 2 : 3-dimethyl ascorbic acid.[94] The latter substance has been converted into the tetramethyl derivative, which on ozonisation and subsequent hydrolysis gives oxalic acid and 3 : 4-dimethyl *l*-threonic acid (III), unaccompanied by the epimeric 3 : 4-dimethyl *l*-erythronic acid. Since a sample of tetramethyl ascorbic acid obtained by direct methylation without separation of the crystalline dimethyl derivative gave both these substances, confirmation is provided for the view previously advanced that ascorbic acid could react in more than one structural modification. There is, however, other evidence in support of this, in

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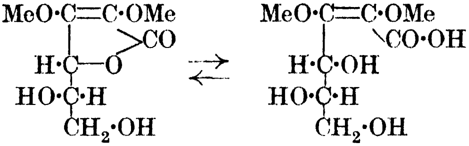
[91] J. M. Gulland, E. R. Holiday, and T. F. Macrae, *J.*, 1934, 1639. See also *Nature*, 1933, **132**, 782 ; *A.*, 8.

[92] E. L. Hirst, *J. Soc. Chem. Ind.*, 1933, **52**, 221; *A.*, 1933, 489; R. W. Herbert, E. L. Hirst, E. G. V. Percival, R. J. W. Reynolds, and F. Smith, *J.*, 1933, 1270; *A.*, 1933, 1143.

[93] T. Reichstein, R. Grüssner, and R. Oppenauer, *Helv. Chim. Acta*, 1934, **17**, 510; *A.*, 633; W. N. Haworth and E. L. Hirst, *ibid.*, p. 520; *A.*, 633.

[94] W. N. Haworth, E. L. Hirst, and F. Smith, *J.*, 1934, 1556.

(IV.)



(V.)

that methylation with one molecular proportion of diazomethane yields, besides (II), a small quantity of an isomeric monomethyl derivative (? 2-methyl ascorbic acid) which is non-reducing and gives but a feeble fleeting colour with ferric chloride. Its physical properties, including absorption spectrum, differ markedly from those of the 3-methyl ether, from which it differs structurally, since it does not give oxalic acid on ozonisation. It can be methylated without structural change, but the dimethyl derivative differs completely from the well-known crystalline 2 : 3-dimethyl ether, into which, however, it is gradually transformed on heating. The position is, therefore, that there is definite evidence of the superior acid character of the 3-hydroxyl group of ascorbic acid, but in view of the above-mentioned complications and of the marked difference in physical properties (*e.g.*, rotatory power) between salts of ascorbic acid and of the 3-methyl derivative the possibility still remains open that salt formation may involve something more than ionisation at the 3-position.

These studies of the methylated derivatives of ascorbic acid have revealed also that the open-chain acid (V), produced by the action of mineral acid on the corresponding sodium or barium salt, lactonises on heating with production of (IV). It is noteworthy that, like other Δ^{α}-unsaturated acids, (V) resists the action of ozone. A further point of interest is that, when 2 : 3-dimethyl ascorbic acid is treated with methyl sulphate and alkali, the sodium salt of a tetramethyl open-chain acid is obtained. This so strongly resists further methylation that it has been suggested that here, and possibly in other cases where γ-hydroxy-groups of sugar acids are difficult to methylate, some connexion is found between this hydroxyl group and the carbonyl group of the acid.

In connexion with the methyl ethers of ascorbic acid reference may be made to the criticisms of Micheel[95] concerning the proof given last year of the structure of the tetramethyl derivative. The latter substance gives after ozonisation a dimethyl threonic acid which was shown to have a free hydroxyl group in the α-position because its amide gave a positive Weerman reaction. The essential feature of the test is that α-hydroxy-amides give sodium cyanate on treatment with sodium hypochlorite, whereas other amides do not. It was claimed by Micheel that the test is not specific for hydroxy-amides but is given also by α-methoxy-amides. Careful repetition of the experiments has, however, shown that this is not the case and that the Weerman test may be applied with confidence to distinguish between α-hydroxy- and α-methoxy-acid amides.[96] During the work certain points have emerged which are of interest in other connexions. Both groups of workers encountered the urethane (VI), produced during the action of hypochlorite on *O*-methylmandelamide in the presence of methyl alcohol, which reacts additively with the *iso*cyanate (VII). The urethane (VI) readily decomposes, giving benzaldehyde, ammonia, methyl alcohol, and carbon dioxide. It seems likely that water acts in a similar manner when the reaction is conducted without the addition of methyl alcohol, leading to an unstable intermediate compound which breaks down with liberation of ammonia, methyl alcohol, and benzaldehyde. This is essentially a Hofmann degradation, complicated in its later stages by the instability of the amine, and it is suggested that the different course of events which occurs when an α-hydroxy-group is present is occasioned by the presence of a co-ordinate link in the intermediate product (VIII), which does not then add on water but breaks down in the presence of alkali to the aldehyde and sodium cyanate.[96]

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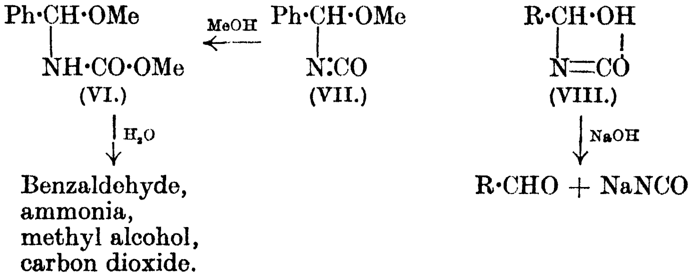
[95] F. Micheel and K. Kraft, *Ber.*, 1934, **67**, [*B*], 841; *A.*, 756.



It is now clear that the *d*-glucosaccharosonic acid of H. Ohle and his collaborators[97] and the *iso*vitamin C of K. Maurer and B. Schiedt[98] are identical and that this substance is the enantiomorph of *l*-arabo-ascorbic acid, obtainable synthetically from *l*-arabinosone. Improved methods of preparation of the *d*-isomeride have been published and the latter is now easily obtainable by the action of sodium methoxide on methyl 2-ketogluconate. Its chemical properties are very similar to those of ascorbic acid and it has been

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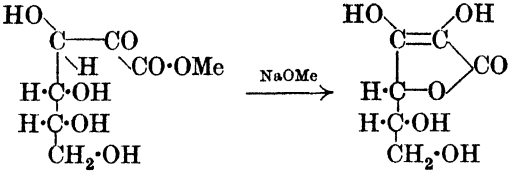
[96] R. G. Ault, W. N. Haworth, and E. L. Hirst, *J.*, 1934, 1722.

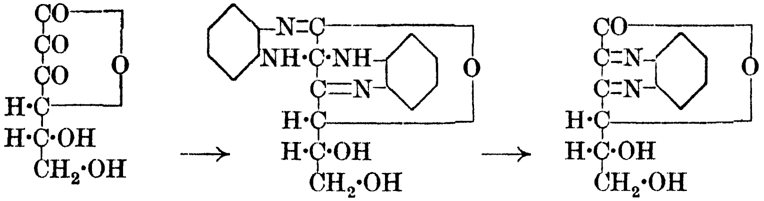
[97] *Ber.*, 1934, **67**, [*B*], 324, 555; *A.*, 392, 634.

[98] *Ibid.*, p. 1239; *A.*, 870.



(IX.)

utilised by Ohle to elucidate the action of phenylhydrazine and *o*-phenylenediamines on substances possessing the ring structure typical of ascorbic acid.[97] Benzoquinone was found to be an excellent oxidising agent, leading to the formation of (X). In aqueous solution in the cold, (X) reacts with *o*-phenylenediamine (2 mols.), giving (XI), which is obtainable also by the direct action of the diamine on arabo-ascorbic acid. In the presence of cold dilute


(X.) (XI.) (XII.)

mineral acids, (XI) is transformed into the quinoxaline derivative (XII), the lactonic character of which is indicated by its transformation, by opening of the ring, into the sodium salt, the amide, and the hydrazide of the corresponding acid. It is of interest to find that on acidification of the sodium salt derived from (XII) both the γ- and the δ-lactone are produced by lactonisation of the open-chain acid. Further evidence concerning the structure of these derivatives is provided by the analogous behaviour of esters of mesoxalic acid.

The lactone (XII) does not react with *o*-phenylenediamine and as a contrast with this series the behaviour of 2-ketogluconic acid towards this reagent may be cited.[99] In this case the substance obtained is the substituted quinoxaline (XIII), which readily breaks down by fission of the molecule, giving dihydroxyquinoxaline with permanganate and yielding glycerol and (XIV) with phenylhydrazine. These investigations throw light on the nature of the reactions between reducing sugars and diamines. For instance, fructose and glucose give a quinoxaline derivative (XV) which closely resembles (XIII) in its properties, but the product obtained with *l*-arabinose is the benziminazole derivative (XVI), characterised by lack of reducing power and stability towards phenylhydrazine.

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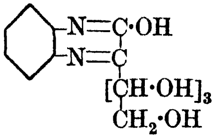
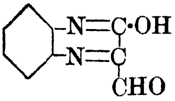
[99] H. Ohle, *Ber.*, 1934, **67**, [*B*], 155; *A.*, 392.

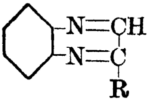
(XIII.)

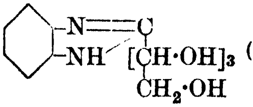




(XIV.)

(XV.)





(XVI.)

In a more recent paper H. Ohle [1] has discussed the nature of the isomerism displayed by the phenylhydrazine derivatives of *l*-ascorbic acid and *d*-arabo-ascorbic acid. It had been shown previously [92] that ascorbic acid on condensation with two molecules of the base gave rise to two well-defined isomeric substances, both of which appeared to be derived from the oxidised form of the acid. The relationship between these has been made clear by a study of the corresponding derivatives of arabo-ascorbic acid. Three compounds are produced by the interaction of phenylhydrazine and *d*-arabo-ascorbic acid, the relative proportion of each depending on the experimental conditions. In the presence of acetic acid the product is mainly the substituted pyrazole (XVII, R = H), whereas with mineral acids little of (XVII) is produced and, instead, a mixture of (XVIII) and (XIX) is obtained. (XVIII) is readily transformed by recrystallisation into (XIX) and (XVII, R = H), and (XIX) is converted by hot dilute alkali solution into the pyrazolone derivative (XVII, R = H). The constitution of (XVII, R = H) follows from the observations that it contains an enolic hydroxyl group and yields a triacetyl *O*-monomethyl derivative from which the crystalline substance (XVII, R = Me) is formed on hydrolysis. Oxidation of (XVII, R = Me) with permanganate in acetone gives (XX), from which (XXI) is obtained by alkaline hydrolysis. This substance (4-benzeneazo-1-phenyl-5-pyrazolone-3-carboxylic acid) gives the ordinary ester (3-carbomethoxy) with methyl-alcoholic hydrogen chloride, whereas with diazomethane it yields the methyl ester of (XX), from which (XX) itself is readily obtainable. The condensation products of the various substances with acetone and with triphenylmethyl chloride are in full accord with the above views. Similar experiments with *l*-ascorbic acid indicate that the yellow derivative, m. p. 210°, corresponds structurally to the pyrazolone (XVII) and the red product, m. p. 197°, is the true osazone (structure as in XIX). Similar views concerning the structure of the yellow derivative have been advanced also by K. Tatematsu, K. Nogi, and A. Yoneda.[2]

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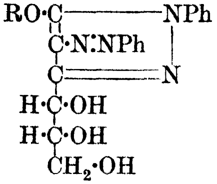
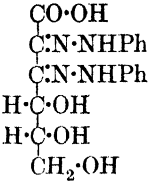
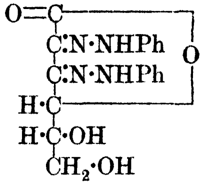
[1] *Ber.*, 1934, **67**, [*B*], 1750.



(XVII.)

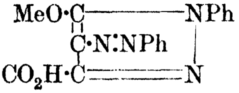


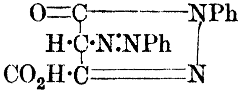
(XVIII.)



(XIX.)

(XX.)





(XXI.)

Very marked progress is to be recorded also on the synthetic side. The three principal methods which are now available are : (1) addition of hydrogen cyanide to an osone, followed by acid hydrolysis of the addition compound; (2) the rearrangement of 2-keto-3 : 4-dihydroxy-acids or their esters, an example of which has been given above in the preparation of arabo-ascorbic acid from 2-ketogluconic acid; (3) oxidation of osones to 2-keto-acids, followed by rearrangement as in method (2). Method (3) is restricted in its scope by the inaccessibility of the necessary osones and the poor yields obtained on oxidation, but it has been employed[3] to effect a synthesis of *l*-ascorbic acid by way of the reactions : *l*-sorbose ⟶ *l*-sorbosazone ⟶ *l*-sorbosone ⟶ 2-keto-*l*-gulonic acid. The last-named substance can then be easily transformed by the methods of Ohle or Maurer into *l*-ascorbic acid. The first method also suffers from the disadvantage of requiring osones as starting material, but when these are available it is a powerful method which has already been used to obtain the following analogues[4] of ascorbic acid, all of which have chemical properties and absorption spectra closely similar to those of natural ascorbic acid : *d*-gluco-ascorbic acid, *d*-galacto-ascorbic acid, *l*-arabo-ascorbic acid, *l*-gulo-ascorbic acid, *d*-xylo-ascorbic acid (*d*-ascorbic acid). The nomenclature used derives the name of the substance from that of the particular osone used in the synthesis.

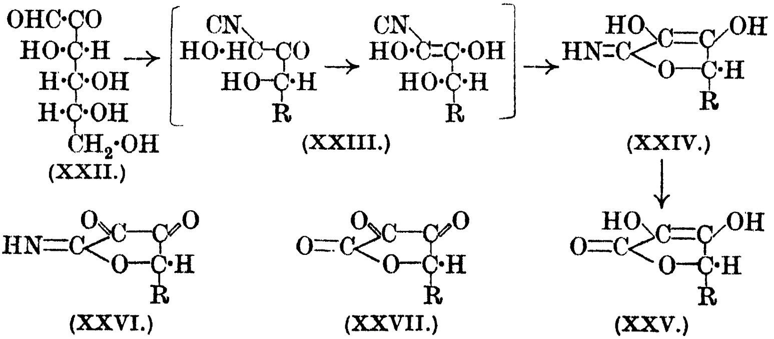
Detailed studies have been made of the mechanism of the synthetic process, the course of which has been elucidated during an investiga-

[2] *Z. physiol. Chem.*, 1934, **225**, 275; *A.*, 1042.

[3] F. Micheel, K. Kraft, and W. Lohmann, *ibid.*, p. 13; *A.*, 869.

[4] R. G. Ault, D. K. Baird, H. C. Carrington, W. N. Haworth, R. Herbert, E. L. Hirst, E. G. V. Percival, F. Smith, and M. Stacey, *J.*, 1933, 1419; *A.*, 1933, 1275; D. K. Baird, W. N. Haworth, R. W. Herbert, E. L. Hirst, F. Smith, and M. Stacey, *J.*, 1934, 62; *A.*, 279; T. Reichstein, A. Grüssner, and R. Oppenauer, *Helv. Chim. Acta*, 1934, **17**, 510; *A.*, 633.

tion of *d*-gluco-ascorbic acid.[5] The first stage of the synthesis from glucosone (XXII) results in the formation of a crystalline addition product, $C_7H_{11}O_6N$, which displays a strong absorption band at λ275 mμ. The properties of this substance indicate that it is not the open-chain cyanohydrin (XXIII) but the cyclic imino-compound (XXIV), which exists in aqueous solution as a neutral internal salt. In neutral solution the high negative rotation of this intermediate compound is very similar to that of salts of *d*-gluco-ascorbic acid (XXV), whereas on addition of acid and suppression of the ionisation of the enolic acidic group, the rotation falls at once to a value close to that of un-ionised *d*-gluco-ascorbic acid. Furthermore, in neutral aqueous solution the intermediate substance displays simple rotatory dispersion and resembles salts of ascorbic acid, but in acid solution the dispersion is anomalous and can be represented by a two-term Drude equation with constants closely similar to those found with ascorbic acid.[6] This change in the character of the rotatory dispersion is highly remarkable and characteristic and provides strong evidence in favour of the structural similarity of the substances concerned. Still further evidence is found in the observation that on oxidation with iodine (XXIV) gives a basic substance (XXVI), from which the imino-group is very readily removed by hydrolysis with formation of the primary oxidation product of *d*-gluco-ascorbic acid (XXVII). On digestion with mineral acid in the cold or with hot aqueous acetic acid, (XXIV) passes smoothly into *d*-gluco-ascorbic acid having an absorption band at λ245 mμ in acid solution. A similar product has been isolated as the intermediate substance in the synthesis of galacto-ascorbic acid and it is clear that the mechanism outlined below for the synthesis of *d*-gluco-ascorbic acid is general for this type of reaction.



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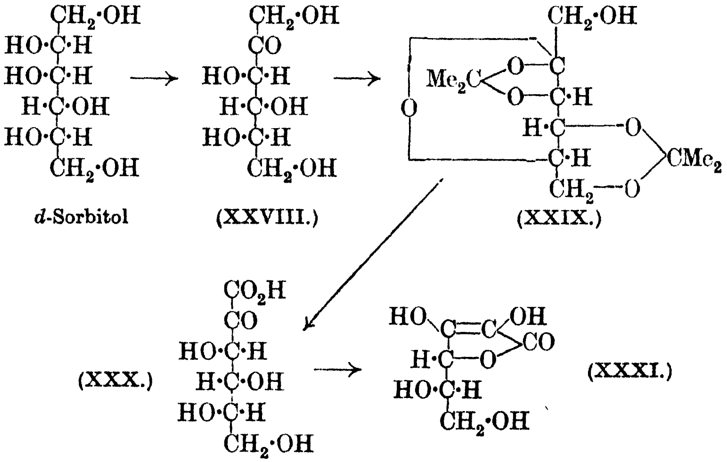
[5] W. N. Haworth, E. L. Hirst, J. K. N. Jones, and F. Smith, *J.*, 1934, 1192; *A.*, 1091.

[6] T. M. Lowry and S. A. Pearman, *J.*, 1933, 1444; *A.*, 1934, 132; R. W. Herbert, E. L. Hirst, and C. E. Wood, *ibid.*, p. 1564; *A.*, 1934, 132.

Notable advances in the ease with which *l*-ascorbic acid can be prepared have resulted from application of the second of the above synthetic methods. The starting point here is *l*-sorbose (XXVIII), which until recently was one of the rarest sugars but may now be obtained in quantity by the action of *B. xylinum* on *d*-sorbitol,[7] the latter substance in turn being derived from *d*-glucose by catalytic hydrogenation. T. Reichstein and A. Grüssner [8] have found that with acetone and sulphuric acid or anhydrous copper sulphate sorbose gives the 2 : 3 : 4 : 6-diacetone derivative (XXIX), the primary alcoholic group of which is attacked by alkaline permanganate, giving the corresponding carboxylic acid. Removal of the acetone groups by boiling water yields 2-keto-*l*-gulonic acid (XXX), from which the methyl ester is easily prepared. When the acid (XXX) is heated with water in the absence of oxygen, partial transformation into *l*-ascorbic acid takes place. A more effective method of carrying out this conversion is to heat the methyl ester of 2-keto-*l*-gulonic acid with sodium methoxide in methyl alcohol. From the sodium salt of *l*-ascorbic acid so obtained, the free acid (XXXI) is easily isolated and by this series of reactions as much as 30 g. of pure *l*-ascorbic acid can be prepared from 100 g. of sorbose.



d-Sorbitol (XXVIII.) (XXIX.)

(XXX.) (XXXI.)

An even simpler and more direct method has recently been described by W. N. Haworth.[9] The primary alcoholic group next to the reducing group of ketoses is peculiarly sensitive to oxidising agents and it has been found that sorbose (XXVIII), when heated under carefully controlled conditions with nitric acid, is transformed directly into 2-keto-*l*-gulonic acid (XXX). The latter substance, which need not be isolated, is esterified by heating it with methyl alcohol, and on addition of sodium methoxide the sodium salt of ascorbic acid is obtained. The same method of direct oxidation by nitric acid is applicable to *d*-fructose and provides a simple method for the preparation of 2-keto-*d*-gluconic acid and hence of *d*-arabo-ascorbic acid.

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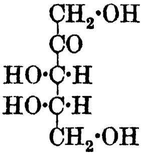
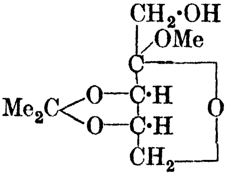
[7] H. Schlubach and J. Vorwerk, *Ber.*, 1933, **66**, [*B*], 1251; *A.*, 1933, 1145.

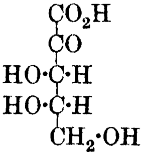
[8] *Helv. Chim. Acta*, 1934, **17**, 311; *A.*, 511.

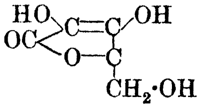
[9] *Nature*, 1934, **134**, 724.

One of the two theoretically possible analogues of ascorbic acid containing five carbon atoms has been synthesised by T. Reichstein,[10] who has obtained *l*-adonose by the oxidative action of bacteria on adonitol. The constitution of this new ketose is established by the observations that it gives *l*-arabinosazone with phenylhydrazine and is transformed into *l*-arabinose by alkali and when heated with pyridine. Methyladonoside gives a monoacetone derivative (XXXIII), which contains a free primary alcoholic group and is readily oxidised by permanganate to the methyl lactolide of 2-keto-3 : 4-monoacetone ribonic acid. Removal of the methyl and acetone groups by gentle hydrolysis gives the free acid (XXXIV), which at once undergoes enolisation and lactonisation with formation of the ascorbic acid analogue (XXXV). The facility with which this complicated transformation is effected is particularly noteworthy in comparison with the behaviour of other 2-keto-acids. The substance (XXXV) (*l*-erythro-ascorbic acid) has the characteristic chemical properties of ascorbic acid, but the possibility of its lactone ring structure being in positions 1 : 5, instead of 1 : 4 as depicted, is not entirely excluded.


(XXXII.)


(XXXIII.)


(XXXIV.)


(XXXV.)

Another compound with properties of more than usual interest is reductic acid (XXXVI), a substance which appears to have been obtained by Thierfelder from glycuronic acid many years ago. It has now been thoroughly investigated by T. Reichstein and R. Oppenauer,[11] who have prepared it by the action of dilute sulphuric acid at high temperatures on various carbohydrates (glycuronic acid, pectin, tetragalacturonic acid, galacturonic acid, xylose). Like ascorbic acid, it is strongly reducing and is reversibly oxidised in acid solution by iodine and dichlorophenolindophenol, giving 1 : 2 : 3-triketo*cyclo*pentane (XXXVII), which with hydrogen sulphide regenerates (XXXVI). (XXXVII) condenses with phenylhydrazine, giving the 1 : 3-diphenylhydrazone and at higher temperatures the triphenylhydrazone. The structure of reductic acid as 3-keto-Δ^1-*cyclo*pentene-1 : 2-diol is shown by its oxidation by silver carbonate to $CO_2H\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$ and by the observation that its diacetate on catalytic hydrogenation gives rise to *cyclo*pentyl acetate and the diacetyl derivative of *cis*-*cyclo*pentane-1 : 2-diol (XXXVIII).

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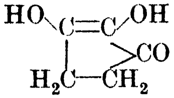
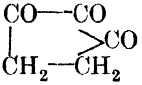
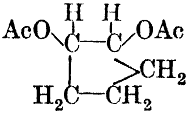
[10] *Helv. Chim. Acta*, 1934, **17**, 996, 1003; *A.*, 1205, 1203.

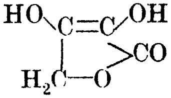
[11] *Ibid.*, 1933, **16**, 988; *A.*, 1933, 1299.

Yet another substance which resembles ascorbic acid in chemical properties is the strongly acidic open-chain compound hydroxy-


(XXXVI.)


(XXXVII.)


(XXXVIII.)


(XXXIX.)

methylglyoxal[12] (reductone), which is formed by the action of alkali on carbohydrates. This triose derivative may well prove to be of considerable importance in connexion with the mode of synthesis of natural products in plant tissues.

The above review shows that in the very short space of time since the elucidation of its structure not only ascorbic acid but also a large number of analogues have been synthesised. The simplest analogue (XXXIX), containing four carbon atoms, has been obtained by F. Micheel and F. Jung[13] from the benzoyl derivative of methyl glycollate. One of the two possible forms containing five carbon atoms is known (*l*-erythro-ascorbic acid). All four possibilities of the C_6 type have been prepared (*d*- and *l*-ascorbic acid; *d*- and *l*-arabo-ascorbic acid) and 3 of the 8 stereoisomeric C_7 substances are known (*d*-gluco-ascorbic acid, *d*-galacto-ascorbic acid, *l*-gulo-ascorbic acid). In addition to these an analogue of ascorbic acid has been prepared from *l*-rhamnosone (*l*-rhamno-ascorbic acid).[13a] A considerable number of ascorbic acid analogues are therefore available for experiment on the correlation of constitution and physiological activity. Synthetic *l*-ascorbic acid has antiscorbutic activity identical with that of the natural product[14] (which can now be obtained in quantity from Hungarian pepper by an improved method of extraction).[15] The primary oxidation product of *l*-ascorbic acid is also fully active,[16] *d*-arabo-ascorbic acid has about $\frac{1}{20}$—$\frac{1}{40}$ the activity of *l*-ascorbic acid [17] and *l*-rhamno-ascorbic acid has about $\frac{1}{5}$ the activity of the natural product.[13a] None of the others referred to above possesses appreciable anti-scorbutic activity. It is possibly significant that the only substances which display antiscorbutic activity are those which have the ring on the right hand side when the structural formula is written in accordance with the Fischer convention [see, *e.g.*, substances (I) and (IX), which are active, and contrast the inactive substances (XXV)].[9]

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[12] R. G. W. Norrish, and J. G. A. Griffiths, *J.*, 1928, 2837; *A.*, 1929, 37; H. von Euler and C. Martius, *Svensk Kem. Tidskr.*, 1933, **45**, 73; *A.*, 1933, 596.

[13] *Ber.*, 1933, **66**, [*B*], 1291; *A.*, 1933, 1143.

[13a] T. Reichstein, *Nature*, 1934, **134**, 724.

[14] W. N. Haworth, E. L. Hirst, and S. S. Zilva, *J.*, 1934, 1155; *A.*, 1091.

Polysaccharides.—Special interest is still centred in the problem of the molecular size of polysaccharides. Estimates of molecular weight derived by different methods (*e.g.*, Staudinger's viscosity method, Svedberg's ultra-centrifuge method, osmotic pressure measurements, and Haworth's chemical method involving quantitative assay of an end-group) are not always in accord and the discrepancies, though not yet fully explained, seem to indicate that a clearer distinction must be drawn in future between the chemical molecule and the variable physical unit which is present in solutions. For instance, strong evidence exists that the amylose and amylopectin fragments of starch have similar chemical molecules and differ from one another in their state of molecular aggregation.[18] Recent work by O. Lamm,[19] using the ultra-centrifuge method, has now shown that amylose and amylopectin are both poly-disperse in solution, the particles of which the former is composed having a mean " molecular weight " of about 60,000 and those of the latter about 300,000. This figure for amylose, although of the same order of magnitude as that given by the viscosity method for ordinary amylose derivatives, is many times greater than that given by the chemical method and it is of particular interest, therefore, to find that a fully disaggregated " amylose " can be prepared and derivatives obtained from it which retain in full the undegraded chemical molecule but exhibit viscosities in exact agreement with the " chemical " molecular size.[20] It may be noted in this connexion that M. Samec and his collaborators, using diffusion and osmotic pressure methods, find " molecular weights " of starch derivatives ranging from 1700 to 500,000 according to the nature of treatment to which the starch has been submitted.[21]

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[15] I. Banga and A. Szent-Györgyi, *Biochem. J.*, 1934, **28**, 1625; *A.*, 1270.

[16] E. L. Hirst and S. S. Zilva, *ibid.*, 1933, **27**, 1271; *A.*, 1933, 1091.

[17] O. Dalmer and T. Moll, *Z. physiol. Chem.*, 1933, **222**, 116; *A.*, 1934, 227; V. Demole, *Biochem. J.*, 1934, **28**, 770; *A.*, 934.

[18] E. L. Hirst, (Miss) M. M. T. Plant, and (Miss) M. D. Wilkinson, *J.*, 1932, 2375; *A.*, 1932, 1116.

[19] *Kolloid-Z.*, 1934, **69**, 44; *A.*, 1172. See also T. Svedberg, *Ber.*, 1934, **67**, [*A*], 117.

[20] W. N. Haworth, *Chem. and Ind.*, 1934, **54**, 1059.

In the case of cellulose recent measurements by A. J. Stamm [22] and by E. O. Kraemer and W. D. Lansing,[23] who made use of the sedimentation–equilibrium method, indicate for native cellulose a molecular weight of about 300,000 (*i.e.*, chain length nearly 2000 glucose units). Difficulties arise here in that cuprammonium solutions of cellulose are highly unstable and the figure quoted is arrived at by extrapolation. The viscosity method with cuprammonium solutions gives a value rather less than half the above (750 units).[24] Here again, however, care is necessary in interpreting the results, not only because of the nature of the solution used, but because difficulties have been encountered in the application of the viscosity method to acetylated and methylated and nitrated derivatives of cellulose.[25] The very high viscosities of methyl celluloses are explained by Staudinger by assuming the formation of co-ordination complexes of the oxonium type between methyl cellulose and *m*-cresol. For cellulose nitrate, which also displays abnormally high viscosities, the same author advances the hypothesis that native cellulose exists as complex esters which are hydrolysed by cuprammonium solution, by mercerisation, and during the purification of technical cellulose, the last process being accompanied by degradation of the molecule.[24] At the other end of the scale, experiments with oligosaccharides [26] serve to support the value of the constants used by Staudinger for molecular-weight calculations, and the validity of the method received general support in the polystyrene series from the sedimentation experiments of R. Signer and H. Gross.[27] Until, however, the above discrepancies are cleared up, no decision can be reached concerning the molecular size of cellulose, for which the chemical method, applied to a derivative of a technical sample, indicates a minimum chain length of 100—200.[28] With reference to the probable existence in solutions of reversible aggregates of the macro-molecules of cellulose derivatives (*e.g.*, nitrate, acetate, ethyl, and benzyl derivatives) the work of S. Glikmann [29] may be consulted, and the character of these aggregates

[21] *Kolloid-Beih.*, 1934, **39**, 421, 438, 464; *A.*, 843.

[22] *J. Amer. Chem. Soc.*, 1930, **52**, 3047, 3667; *A.*, 1930, 1248.

[23] *Nature*, 1934, **123**, 870; *A.*, 760.

[24] H. Staudinger, *Cellulosechem.*, 1934, **15**, 53, 65; *A.*, 760.

[25] H. Staudinger and H. Scholz, *Ber.*, 1934, **67**, [*B*], 48; *A.*, 283; G. L. Wilson and F. D. Miles, *Phil. Trans.*, 1934, [*A*], **233**, 247.

[26] H. Staudinger and E. O. Leupold, *Ber.*, 1934, **67**, [*B*], 479; *A.*, 514.

[27] *Helv. Chim. Acta*, 1934, **17**, 59, 335, 726; *A.*, 361, 504, 986.

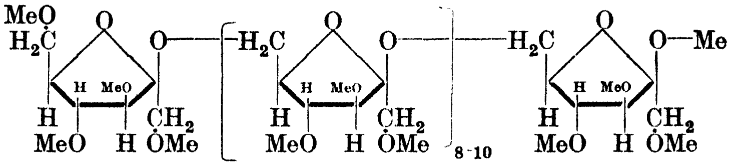
[28] W. N. Haworth and H. Machemer, *J.*, 1932, 2270; *A.*, 1932, 1022.

[29] *J. Chim. physique*, 1934, **31**, 458; *A.*, 1069.

(micelles) as they exist in natural fibres has been utilised by E. Elöd and H. Schmid-Bielenberg[30] to explain the varying rates of acetylation exhibited by cotton, ramie, hemp, and flax.

It is of interest to note the identity of chemical structure of all celluloses hitherto examined, whether of animal or of vegetable origin. Evidence in the case of animal cellulose (tunicin prepared from *Phallusia mammilaris*) has been obtained by partial acid hydrolysis, which gives rise to dextrins, cellobiose, a triose, a tetraose, and a hexaose (regarded by Staudinger[26] as probably a pentaose), all of which are identical with the corresponding products from cellulose and indicate, therefore, identity of structure in the parent substances.[31] Bacterial celluloses obtained from fructose, glycerol, and glucose respectively have been examined by J. Barsha and H. Hibbert, who conclude from comparison of acetyl and methyl derivatives, *X*-ray examination, and degradation reactions that all three bacterial celluloses are similar in structure to ordinary cotton cellulose.[32]

Polysaccharides based on fructose have given rise to problems of special interest. The levan obtained by the action of *B. mesentericus* on sucrose has been shown to consist of chains of fructofuranose units joined through positions 2 and 6,[33] in contrast with inulin where the chains of fructofuranose units are connected through positions 1 and 2. The chain length of the methylated derivative of this levan has now been estimated, by quantitative assay of the terminal group, which gives rise to 1 : 3 : 4 : 6-tetramethyl fructofuranose on hydrolysis, to be 10—12 fructofuranose units.[34]



Yields 1 : 3 : 4 : 6-tetramethyl fructofuranose

Yields 1 : 3 : 4-trimethyl fructofuranose

W. Mitchell and H. Hibbert find that the levan obtained by bacterial action on the trisaccharide raffinose has the same structure as that from sucrose and conclude that a potential fructofuranose residue must be present in any material convertible into levan by

[30] *Z. physikal. Chem.*, 1934, [*B*], **25**, 27; *A.*, 606.

[31] L. Zechmeister and G. Toth, *Z. physiol. Chem.*, 1933, **215**, 267; *A.*, 1933, 381.

[32] *Canadian J. Res.*, 1934, **10**, 170; *A.*, 515.

[33] H. Hibbert, R. S. Tipson, and F. Brauns, *ibid.*, 1931, **4**, 221; *A.*, 1931, 827.

[34] S. W. Challinor, W. N. Haworth, and E. L. Hirst, *J.*, 1934, 676; *A.*, 760.

B. mesentericus.[35] More recently S. W. Challinor, W. N. Haworth, and E. L. Hirst [36] have found in meadow grass a polysaccharide which is apparently identical with the above levan. The chemical and physical properties of the polysaccharide disclose its similarity to levan, and its methylated derivative gives rise on hydrolysis to 1 : 3 : 4-trimethyl fructofuranose. It is clear, therefore, that in plant life reserve carbohydrate may be stored as chains of fructofuranose units in at least two ways : (*a*) as the inulin type (junction 1 : 2), and (*b*) as the levan type (junction 2 : 6). No example is yet known of the occurrence of fructopyranose units in a natural polysaccharide, whereas glucose units appear invariably in the pyranose form. The only disaccharide which could be identified with any certainty in the grass extract was gentiobiose, but sucrose may well have been present in the living plant.

The possibility of the existence of 2 : 4-anhydrides of fructofuranose in polysaccharides is suggested in the work of H. H. Schlubach, H. Knoop, and M. Y. Liu [37] on the constitution of irisin. Controlled hydrolysis of the latter with sulphuric acid leads to the formation of a di-irisan, which on methylation yields a methyl derivative. This on hydrolysis gives rise to equivalent amounts of 1 : 3 : 4 : 6-tetramethyl fructofuranose and dimethyl fructose (possibly the 3 : 6-derivative). Partial hydrolysis of di-irisan results in the formation of an intermediate product, which after methylation and hydrolysis yields a trimethyl fructose, which is not the 3 : 4 : 6-derivative and has one of its methyl groups in position 1. On the other hand, the dimethyl fructose gives an osazone without loss of a methyl group and must therefore have position 1 vacant.

Much progress is to be reported in the study of the mannans present in ivory nut. When the nut shavings are extracted with water and acetone, treated with chlorine dioxide, and then extracted with dilute aqueous sodium hydroxide, addition of acetic acid to the alkaline solution precipitates mannan-A, from which the fully methylated derivative is obtained by means of methyl sulphate and alkali. Hydrolysis of methylated mannan-A gives rise to crystalline 2 : 3 : 6-trimethyl mannose, accompanied by a small quantity (1—1·4%) of 2 : 3 : 4 : 6-tetramethyl mannopyranose. By partial hydrolysis, methylated mannobiose and mannotriose derivatives have been obtained, which after methylation and subsequent hydrolysis give rise to 2 : 3 : 4 : 6-tetramethyl mannopyranose and 2 : 3 : 6-trimethyl mannose. It follows that mannan consists of a terminated chain of consecutive units of mannopyranose linked through positions 1 and 4, as are the glucose residues in cellulose.

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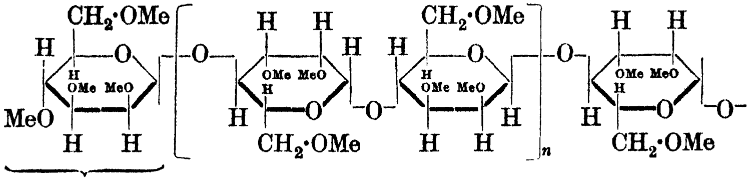
[35] *Canadian J. Res.*, 1932, **7**, 345; *A.*, 1933, 148. [36] *J.*, 1934, 1560.

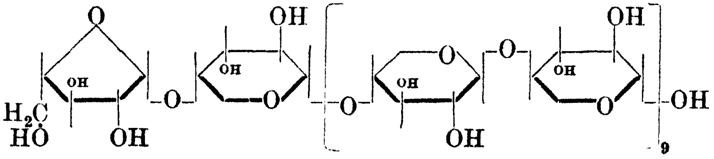
[37] *Annalen*, 1934, **511**, 140; *A.*, 873.

From the yield of tetramethyl mannopyranose, the chain length of methylated mannan is estimated to be about 80 mannose residues. Mannan-B is similarly constituted.[38]



(*Note*: α- as well as β-mannosidic links may be present in the molecule)

A new phase in the investigation of xylan has been opened up by the discovery that this polysaccharide, which occurs extensively in woody tissues and forms some 30% of esparto cellulose, is not composed entirely of xylose residues but contains combined arabinose. The proportion of arabinose was the same in the several samples of xylan examined and the possibility now exists that xylan is to be regarded as more closely related to the natural gums than to cellulose. Investigations into the mode of linkage of the arabinose revealed that it was present as arabofuranose, this being the first recorded instance of the natural occurrence of an arabofuranose derivative. Since methylated xylan gave on hydrolysis 6% of 2 : 3 : 5-trimethyl arabofuranose (the identity of which was established by its transformation into the corresponding well-known crystalline lactone), it follows that the arabinose is a terminal unit associated with about 16 xylose units. Evidence has already been provided which shows that the xylose units are pyranose in structure and the simplest structure for methylated xylan is therefore the one represented below. At this stage, however, other more complex structures cannot be



definitely ruled out, since the nature of the other terminal group is unknown and the 2 : 3-dimethyl xylose which forms the main hydrolysis product of methylated xylan is accompanied by a small quantity of monomethyl xylose, the origin of which is at present obscure. Alternative terminated chain structures, containing consecutive xylopyranose units having an arabofuranose residue attached as a side chain at approximately every 16th xylose residue, and also continuous rings of xylopyranose residues with arabofuranose units as side chains, have been discussed by the authors and will be found figured in the original paper.[39]

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[38] F. Klages, *Annalen*, 1934, **509**, 159; **512**, 185; *A.*, 514, 1093.

A few points of special interest in polysaccharide chemistry may be very briefly discussed in conclusion. Attention is drawn to the remarkable polysaccharide galactogen, which occurs in certain snails and snails' eggs. The only carbohydrate obtained from it on hydrolysis is galactose and it appears to contain both phosphorus and iron as integral parts of the molecule.[40] Certain important methods of degradation applicable to polysaccharides should also be mentioned. For instance, dry hydrogen chloride has been found to react with dry cellulose, giving as an intermediate product 1-chloroglucose, and methylated cellulose similarly gives rise to 2 : 3 : 6-trimethyl α-chloroglucose.[41] Of interest also is the use of the tri-*p*-toluenesulphonyl derivative of starch and its conversion by hydrogen bromide in acetic acid into an acetylated derivative of 2 : 3 : 6-tri-*p*-toluenesulphonyl α-bromoglucose.[42] The methods of thermal degradation studied by E. Berner and his collaborators [43] are of wide utility and have been applied to starch, glycogen, lichenin, and inulin. It is found, for example, that when starch is heated with glycerol the degradation products (dextrins) contain glycerol combined as the glucoside and on continued heating the products are α- and β-glycerylglucosides. Other polysaccharides behave similarly. Methyl alcohol reacts similarly at a high temperature and under pressure, methylated starch being completely hydrolysed by this procedure and giving rise to a mixture of the α- and the β-form of 2 : 3 : 6-trimethyl methylglucopyranoside.

E. L. H.
S. P.

H. D. K. Drew.
E. L. Hirst.
R. S. Morrell.
S. Peat.

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[39] W. N. Haworth, E. L. Hirst, and E. Oliver, *J.*, 1934, 1917.

[40] F. May, *Z. Biol.*, 1934, **95**, 277; *A.*, 914.

[41] H. H. Schlubach and V. Prochownick, *Angew. Chem.*, 1934, **47**, 132; *A.*, 396.

[42] K. Hess and R. Pfleger; K. Hess, O. Littmann, and R. Pfleger; K. Hess and O. Littmann, *Annalen*, 1933, **507**, 48, 55; *Ber.*, 1934, **67**, [*B*], 465; *A.*, 1933, 1279; 1934, 514.

[43] *Annalen*, 1932, **500**, 52; **505**, 58; *A.*, 1932, 150, 938; *K. Norske Vidensk. Selsk. Forhandl.*, 1933, **5**, 167; **6**, 1; *A.*, 1933, 380; 1934, 1207; *Ber.*, 1933, **66**, [*B*], 1333; *A.*, 1933, 1146.

PART II.—HOMOCYCLIC DIVISION.

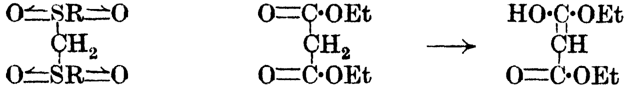
Keto-Enol Tautomerism and Ester Condensations.

(Continued from *Ann. Reports*, 1929, **26**, 116.)

IN spite of the large amount of work devoted to keto-enol tautomerism in the past,[1] the relationship between structure and tendency to tautomerism in its various manifestations is but hazily defined.

A notable attempt to systematise our outlook is that of F. Arndt and C. Martius,[2] who consider at length the connexion between acidity and enolisation. The authors largely disregard the theoretical treatment of the subject by chemists in this country; for this reason their terminology is retained in the present brief account.

Arndt and Martius term the tendency for the change from the ketonic to the enolic form, $CH{\cdot}C{:}O \longrightarrow C{:}C{\cdot}OH$, the enotropic effect of the molecule, and the work done in the transference of the proton from C to O is the prototropic expenditure of work. The tendency to enolisation (*i.e.*, the free energy of enolisation in the gas phase; compare p. 197) is therefore proportional to the enotropic effect and inversely proportional to the prototropic expenditure of work. The acidity of a compound depends solely on the ease of removal of the proton; this can be promoted by the effect of suitable groups attached to the atom carrying the hydrogen atom. These act by diminishing the prototropic expenditure of work and it is shown that some groups possessing no enotropic effect can exert a strong "acidifying" action. Such a group is sulphonyl, SO_2: the ester $CH_2(SO_2R)_2$ is soluble in alkalis and is methylated by diazomethane, but it is incapable of enolisation because the sulphonyl group does not contain a double bond; this is only possible in such groups as carbonyl and carbethoxyl:



$$\begin{array}{c}O\overset{\leftharpoonup}{=}SR\overset{\rightharpoonup}{=}O\\ |\\ CH_2\\ |\\ O\overset{\leftharpoonup}{=}SR\overset{\rightharpoonup}{=}O\end{array}\qquad\begin{array}{c}O{=}C{\cdot}OEt\\ |\\ CH_2\\ |\\ O{=}C{\cdot}OEt\end{array}\longrightarrow\begin{array}{c}HO{\cdot}C{\cdot}OEt\\ \|\\ CH\\ |\\ O{=}C{\cdot}OEt\end{array}$$

Translated into modern electronic terminology, the distinction is between an inductive (— *I*) effect, due to the presence of a pole, and an electromeric (— *T*) effect, depending on polarisability.

The order of the acidifying effect of groups is therefore not the same as that of their enotropic effect; the former is $SO_3R >$

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[1] The older work is adequately reviewed by W. Hückel, "Theoretische Grundlagen der Organischen Chemie," 2nd Ed., Leipzig, 1934, pp. 215 *et seq.*

[2] *Annalen*, 1932, **499**, 228; *A.*, 1933, 146.

$SO_2R > CO_2R > CHO > COR$, and the latter is $CHO > COR > CO_2R$.* The position of the carbethoxyl group is noteworthy: its greater acidifying effect, in spite of the lower enotropic effect, is well exemplified by a comparison of the compounds $CH(CO_2Et)_3$ and $CH(COMe)_3$.

The formation of a sodio-derivative from the non-enolised malonic ester is explained in the same way; the mobile hydrogen remains attached to carbon until it is removed. The structure of metallic derivatives is also discussed; they are regarded as ionic compounds.

Methylation with diazomethane is largely used by the authors in support of their arguments and its use is extended to the determination of the structure of such compounds as saccharin, phthalimide, sulphinic acids, etc.[3]

The conception that alkylation proceeds through a common electromeric anion disposes of the necessity for assuming alkylation on oxygen, followed by isomerisation of the *O*-alkyl compound into the *C*-alkyl, which is still maintained by A. Hantzsch.[4] An interesting experiment by F. Adickes, G. v. Hessling, and S. v. Müllenheim [5] also shows that such a mechanism is improbable: the methylation of ethyl malonate and the ethylation of methyl malonate should lead to the intermediate formation of the acetals $CO_2R{\cdot}CH{:}C(OMe)(OEt)$, in which the alkyl groups should have the same *relative* opportunity of migrating to the central carbon atom. The same alkylation product (or mixture of two alkylation products) should therefore be formed in the two cases: actually ethylation gives the pure ethyl-, and methylation the pure methyl malonic ester.

The result can, of course, be interpreted in the light of the widely held view [1] that small amounts of the *C*-metallic derivative are present in equilibrium with the enolate and are responsible for alkylation in virtue of their great reactivity; the question really resolves itself into the *time* of the redistribution of the anionic charge.

Degree of Enolisation and Structure of Enols.—Although a good deal of evidence has been accumulated as the result of purely chemical work (such as oxidation, fission with alkali, etc.), the interpretation of the results requires caution when dealing with mobile tautomeric systems, and many investigators have preferred purely physical methods, which cannot disturb the system and are therefore trustworthy, provided the results can be interpreted with certainty. That this is not always the case is apparent from the conflicting data obtained by different methods.

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[3] F. Arndt and H. Scholz, *Annalen*, 1934, **510**, 62; *A.*, 770.

[4] *Z. anorg. Chem.*, 1932, **209**, 215; *A.*, 1933, 142.

[5] *Ber.*, 1933, **66**, [*B*], 826; *A.*, 1933, 697; compare also F. Adickes, *ibid.*, p. 1984, and G. Wanag, *ibid.*, p. 1678; *A.*, 1934, 171, 77.

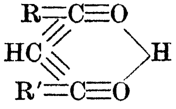
* The difference between acidity and degree of enolisation is strikingly shown by a comparison of ethyl *cyclo*pentanonecarboxylate with the *cyclo*hexane compound; the former is more acid but less extensively enolised (W. Dieckmann, *Ber.*, 1922, **55**, 2470; *A.*, 1922, i, 1020).

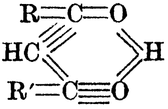
R. A. Morton and his associates [6] have studied the absorption spectra of benzoylacetone, its *O*- and *C*-derivatives, and numerous related compounds. Their results indicate that the enolic form of benzoylacetone, which predominates in solutions in hydrocarbons, etc., is COPh·CH:C(OH)Me, although the sodio-derivative may probably be derived from the alternative enol C(OH)Ph:CH·COMe, at any rate in very dilute solutions; this observation supports the view expressed by A. Michael and J. Ross [7] on the strength of the reaction of the sodio-derivative with ethyl chloroformate.

The sodio-derivative in presence of excess of sodium ethoxide is regarded as chelated, but there appears to be no chelation in the free enol, unless this is of a different type from that obtaining in the sodio-derivative.

The enol of the β-methyl compound differs in the character of the absorption spectrum from the parent compound and is formulated as CPh(OH):CMe·COMe; since, however, the chelated sodio-derivatives of both enols have very similar absorptions, it is suggested that in the process of chelation the difference in structure disappears. This is to be expected on S. Sugden's singlet linkage formula (I),[8] but not on N. V. Sidgwick's earlier formulation (II): [9]

(I.)





(II.)

The latter conception has, however, since been modified; the facts are, of course, compatible with the more modern view that chelation is an attachment of the hydrogen alternately to one or other oxygen by resonance.[9a]

The dienolic form of benzoylacetone can exist only in very small amounts, although the formation of a disodio-derivative of this form is not precluded. The existence of dienols was originally postulated to account for the results of ozonisation,[10] but these are not conclusive, if only because ozonisation is a slow process as compared with the rate of equilibration of most keto-enol systems; [11] in a refractometric reinvestigation of the problem K. v. Auwers [12] suggests that the existence of dienols in any quantity is improbable.

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[6] R. A. Morton, A. Hassan, and T. C. Calloway, *J.*, 1934, 883; *A.*, 1005; R. A. Morton and W. C. V. Rosney, *ibid.*, 1926, 706; R. A. Morton and E. Rogers, *ibid.*, p. 713; *A.*, 1926, 454.

[7] *J. Amer. Chem. Soc.*, 1931, **53**, 2394; *A.*, 1931, 1035.

[8] *J.*, 1929, 316; *A.*, 1929, 427.

[9] *J.*, 1925, **127**, 907; *A.*, 1925, i, 630.

[9a] N. V. Sidgwick, *Ann. Reports*, 1933, **30**, 112. The Reporter is indebted to Prof. T. M. Lowry, F.R.S., for drawing his attention to an earlier paper by himself and H. Burgess (*J.*, 1923, **123**, 2111), in which it is pointed out that the two possible enols of such diketones as benzoylcamphor are identical, the mobile hydrogen being regarded as co-ordinated.

Dibenzoylmethane and ethyl benzoylacetate also appear to be unchelated, in contrast to their sodio-derivatives.[6]

The absorption spectra of the two forms (keto and enol) of benzylmethylglyoxal have been determined by T. M. Lowry, H. Moureu, and H. A. C. McConkey,[13] who have also examined benzoylacetone, though in less detail; and the absorption spectra of the two forms of benzoylcamphor and of their equilibrium mixture have been studied.[14] This compound is convenient because the two forms are comparatively stable and a check on the spectrographic results is afforded by the optical activity of the material. The equilibrium mixture in alcohol contains about $\frac{2}{3}$ of enol at the dilution required for spectrographic work; the figure 58—59% for high concentrations is derived both from solubility determinations on the enol and from polarimetric measurements.

The infra-red spectra of benzoyl- and acetyl-acetone show the characteristic bands due to the C:O group, but no bands attributable to a hydroxyl group.[15] This may be due to an unexpectedly large displacement owing to the proximity of the double bond, or to the abnormal vibration of the (mobile) hydrogen of the hydroxyl group in these compounds.

The Raman spectra of ethyl acetoacetate and a number of related compounds have been measured,[15a] but the interpretation of the results does not appear to be simple, although the effect of enolisation is clearly shown.

The degree of enolisation of β-ketonic esters and β-diketones is greatly influenced by the "solvent effect," and this is, of course, observed in the pure liquid and obscures the effects due to changes in constitution. A true criterion of the latter is afforded by the free energy of enolisation, which was determined for a number of examples by J. B. Conant and A. F. Thompson.[16] The measurements were made at a low pressure in the gaseous phase, the liquid phase being used as an intermediary, since interconversion in the gas phase is very slow; the constant composition of the distillate indicates that equilibrium conditions were maintained. The effect of changes of structure on the equilibrium observed in the gas phase was much more regular than that observed in solvents, the best of the latter being hexane. The effect was, generally speaking, of the type expected; for instance, secondary alkyl groups decrease enolisation more than primary ones, but the phenyl group has a marked effect in the opposite direction. The acetyl group promotes enolisation more than carbethoxyl, but no simple additive relationship exists, probably owing to chelation of the enols; this is supported by the greater volatility of the enolic form in every case.

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[10] J. Scheiber and P. Herold, *Annalen*, 1914, **405**, 295; *A.*, 1914, i, 926.

[11] A. Michael and J. Ross, *J. Amer. Chem. Soc.*, 1931, **53**, 2394; *A.*, 1931, 1035; K. v. Auwers, *Ber.*, 1933, **66**, [*B*], 955; *A.*, 1933, 810.

[12] *Loc. cit.*

[13] *J.*, 1928, 3167; *A.*, 1929, 189.

[14] T. M. Lowry, H. Burgess, and H. A. C. McConkey, *ibid.*, p. 1333; *A.*, 1928, 766.

[15] C. E. H. Bawn, *J.*, 1932, 1189; *A.*, 1932, 558.

[15a] K. W. F. Kohlrausch and A. Pongratz, *Ber.*, 1934, **67**, [*B*], 976, 1465; *A.*, 869, 1205.

An ingenious method for the study of the rate of enolisation under the influence of various catalysts is due to J. B. Conant and G. H. Carlson,[17] who measured the rate of racemisation of several optically active β-diketones; the large differences in the activities of different catalysts, ranging from sodium methoxide in *tert.*-butyl alcohol, which was 2000 times more effective than piperidine, to hydrogen chloride, which was 1000 times less effective, may be noted.

By rigid exclusion of catalytic impurities it is possible to obtain enolic acetoacetic ester with a half-life period of 500 hours.[18] For the preparation of esters of high enol content the slow distillation of acylacetic esters is recommended,[19] but the higher homologues are less completely enolised; for instance, the enol content of ethyl butyrylacetate only rises to 64% and that of ethyl valerylacetate to 34%, although the initial enol content of these esters is somewhat higher than that of ethyl acetoacetate (*e.g.*, ethyl hexoylacetate contains 16·3% of enol).

The relationship between the fission of β-diketones and β-ketonic esters and their constitution has formed the subject of much work by H. Adkins and his collaborators.[20–25] There is a proportionality between the rate of fission by alcoholic hydrogen chloride and the extent of enolisation of the compound in alcohol;[20] this proportionality is reversed with alcoholic sodium ethoxide.[22] These observations support the view, put forward some time ago, that alkaline fission takes place in the ketonic phase,[26] especially as diketones incapable of enolisation are very readily split. Against that, it has also been found that a compound fixed in the enolic form readily undergoes fission.[27] Ketonic esters undergo alkaline fission less easily than β-diketones.[22] Substitution at the middle carbon atom in the latter promotes alkaline fission,[24] as would be expected, since this also reduces the extent of enolisation; in the experiments with sodium ethoxide and other alkaline reagents, however, a proportion of the catalyst is removed with the formation of the metallic enolate, and this must affect the result to a greater or less extent.

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[16] *J. Amer. Chem. Soc.*, 1932, **54**, 4039; *A.*, 1932, 1203.

[17] *Ibid.*, p. 4048; *A.*, 1932, 1251.

[18] F. O. Rice and J. J. Sullivan, *ibid.*, 1928, **50**, 3048; *A.*, 1929, 48.

[19] J. Décombe, *Ann. Chim.*, 1932, **18**, 81; *A.*, 1933, 50.

[20] H. Adkins, W. M. Kutz, and D. D. Coffman, *J. Amer. Chem. Soc.*, 1930, **52**, 3212; *A.*, 1930, 1273.

[21] H. Adkins and W. M. Kutz, *ibid.*, p. 4036; *A.*, 1930, 1559.

[22] *Idem*, *ibid.*, p. 4391; *A.*, 1931, 69.

[23] H. Adkins and R. Connor, *ibid.*, 1932, **54**, 3420; *A.*, 1932, 1020.

[24] H. Adkins, R. N. Isbell, and B. Wojcik, *ibid.*, p. 3678; *A.*, 1932, 1112.

[25] H. Adkins and L. J. Beckham, *ibid.*, 1934, **56**, 1119; *A.*, 759.

The connexion between the ratio of the quantities of the two possible acid products of fission of a diketone and the strengths of the acids [26] does not hold in every case.[21] Alcoholysis at high temperatures with and without an added catalyst has also been examined.[23] The results are correlated in the last paper and an electronic mechanism is suggested both for acid and for alkaline fission; [25] the paper does not lend itself to a concise summary, but the salient features of the previous work are satisfactorily explained; the effect of substituents is shown to be in accordance with their known inductive and electromeric effects ($\pm I$ and $\pm T$).

The alkaline fission of β-diketones and β-ketonic esters amounts in effect to a reversal of the Claisen reaction by which they are obtained; the reversibility of this reaction has long been known, but additional determinations of the position of equilibrium have lately been made.[28] The equilibrium mixtures obtained from alkyl acetates in presence of sodium alkoxides contain much more of the keto-ester (about 66%) than was formerly supposed.[29] The acetates diminish in activity from those of primary to those of tertiary alcohols; this does not, however, affect the final equilibrium to a great extent.

High yields of ethyl acetoacetate are obtained by removing the alcohol formed in the reaction, as might be expected.[30]

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[26] W. Bradley and R. Robinson, *J.*, 1926, 2356; *A.*, 1926, 1145.

[27] L. F. Fieser, *J. Amer. Chem. Soc.*, 1929, **51**, 940; *A.*, 1929, 567.

[28] N. Fisher and S. M. McElvain, *ibid.*, 1934, **56**, 1766; *A.*, 1091.

[29] L. A. Higley, *Amer. Chem. J.*, 1907, **37**, 299; *A.*, 1907, i, 461; H. Adkins and W. M. Kutz, *J. Amer. Chem. Soc.*, 1930, **52**, 4392; *A.*, 1931, 69; J. M. Snell and S. M. McElvain, *ibid.*, 1931, **53**, 2310; *A.*, 1931, 1035.

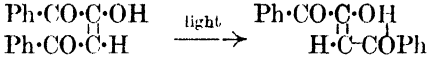
[30] S. M. McElvain, *ibid.*, 1929, **51**, 3124; *A.*, 1929, 1424.

Interesting compounds from the point of view of keto-enol tautomerism are the triketones of the type $\mathrm{Ph{\cdot}CO{\cdot}CO{\cdot}CH_2{\cdot}COPh}$ lately investigated by R. E. Lutz and his collaborators.[31–35]

The keto-forms, which are simultaneously 1 : 2-, 1 : 3-, and 1 : 4-diketones, are only known in some cases, such as the dimesityl compound;[32] the enols (diaroylethenols) are obtained in the form of their alkyl ethers by the action of sodium alkoxides on diaroylacetylenes or the corresponding dibromides and further hydrolysis

$$\begin{tikzcd}
\mathrm{COPh{\cdot}C{\vdots}C{\cdot}COPh + NaOMe} \arrow[r] & \mathrm{COPh{\cdot}C(OMe){:}CH{\cdot}COPh} \arrow[d] & \text{(I.)} \\
\mathrm{COPh{\cdot}CBr{:}CBr{\cdot}COPh + NaOMe} \arrow[ur] & \mathrm{COPh{\cdot}C(OH){:}CH{\cdot}COPh} &
\end{tikzcd}$$

then gives the free enol :[34] this occurs in a coloured (yellow) and a colourless modification, the former being the more stable. The authors regard them as stereoisomerides; the more volatile and soluble yellow form is designated as the *trans*, in which chelation is possible :

(II.)  (III.)

$$\begin{array}{c}\mathrm{Ph{\cdot}CO{\cdot}C{\cdot}OH}\\ \|\\ \mathrm{Ph{\cdot}CO{\cdot}C{\cdot}H}\end{array} \xrightarrow{\text{light}} \begin{array}{c}\mathrm{Ph{\cdot}CO{\cdot}C{\cdot}OH}\\ \|\\ \mathrm{H{\cdot}C{-}COPh}\end{array}$$

There is evidence for the existence of the alternative form of the enol (IV), for, although alkylation by diazomethane gives solely the ether (I), the isomeric ethers of type (IV) are obtained by the action of alcoholic hydrogen chloride on dibenzoylacetylene or its hydrochloride :

$$\mathrm{Ph{\cdot}CO{\cdot}C{\vdots}C{\cdot}COPh + R{\cdot}OH + HCl \longrightarrow Ph{\cdot}CO{\cdot}CO{\cdot}CH{:}C(OR)Ph} \quad \text{(IV.)}$$

Alkylation of the enols (II) and (III) through their sodio-derivatives also leads to the *O*-ethers of type (IV), the structure of which is established by oxidation. This behaviour may be attributed to chelation, which would obliterate the difference between the two enolates (compare p. 195).

The behaviour of dibenzoylethenol on reduction,[35] in which it resembles the ethers of type (I), is held to be incompatible with its existence in the form $\mathrm{Ph{\cdot}CO{\cdot}CO{\cdot}CH{:}C(OH)Ph}$, although it may be doubted whether it is justifiable to regard such a system as static in one modification; its behaviour with various alkylating agents points to considerable mobility.

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[31] J. B. Conant and R. E. Lutz, *J. Amer. Chem. Soc.*, 1925, **47**, 881; *A.*, 1925, i, 681.

[32] R. E. Lutz, *ibid.*, 1926, **48**, 2905; *A.*, 1927, 58.

[33] *Idem*, *ibid.*, 1934, **56**, 1590; *A.*, 1005.

[34] R. E. Lutz, F. N. Wilder, and C. I. Parrish, *ibid.*, p. 1980; R. E. Lutz and F. N. Wilder, *ibid.*, p. 1987; *A.*, 1222.

[35] R. E. Lutz and F. N. Wilder, *ibid.*, p. 2065; *A.*, 1356.

Bis(trimethylbenzoyl)ethenol, which is only known in one enolic form,[33] gives with diazomethane two isomeric ethers, which differ in colour like the enols discussed above; they are interconvertible in the presence of sodium methoxide, and light converts the coloured into the colourless form. Here again the yellow form is given the *trans*-configuration, like the parent enol; the latter is, however, regarded as chelated, whereas chelation is impossible in the ether, a difference which may well affect the validity of the argument.

Mechanism of the Claisen Reaction.—Attempts to devise a satisfactory explanation of the acetoacetic ester condensation have been made for many years and some interesting results have lately been achieved by the application of a more refined experimental technique.

In all the classical schemes, such as Claisen's and Dieckmann's,[36] the fundamental assumption was made that the molecule carrying the metal is integrally added to a molecule of ester, which eventually supplies a hydrogen atom to enable a molecule of alcohol to be eliminated, forming sodioacetoacetic ester. A radical departure from this was proposed by H. Scheibler,[37] who suggested that it is the molecule carrying the sodium which loses hydrogen:

$$\underset{\text{(I.)}}{CH_2{:}C(ONa)OEt} + Me{\cdot}CO{\cdot}OEt \longrightarrow \underset{\text{(II.)}}{Me{\cdot}CO{\cdot}CH_2{\cdot}C(OEt)_2{\cdot}ONa}$$

He and J. Voss had previously [38] experimentally demonstrated the formation of metallic enolates such as (I); he and H. Ziegner [39] also found that the so-called primary addition product (II) gave on decomposition with water, apart from ethyl acetoacetate, keten acetal, $CH_2{:}C(OEt)_2$, and sodium acetate.

Scheibler's scheme explains at once why ethyl benzoate reacts with sodium only on the addition of ethyl acetate, and enables us to formulate such reactions as the condensation of ethyl oxalate with fluorene and of ethyl trifluoroacetate with ethyl acetate.[40]

In H. Lux's condensation of the sodio-derivative of acetone with ethyl carbonate,[41] the first product should be Scheibler's addition compound (II):

$$CMe(ONa){:}CH_2 + CO(OEt)_2 \longrightarrow Me{\cdot}CO{\cdot}CH_2{\cdot}C(ONa)(OEt)_2$$

the product obtained actually yielded ethyl acetoacetate on decomposition with water.

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[36] An excellent summary of the development of the problem is given by G. W. Tschelinzew, *Ber.*, 1934, **67**, [*B*], 955; *A.*, 868.

[37] *Z. angew. Chem.*, 1923, **36**, 6; *Ber.*, 1926, **59**, 1022; *A.*, 1926, 711.

[38] *Ber.*, 1920, **53**, 388; *A.*, 1920, i, 366.

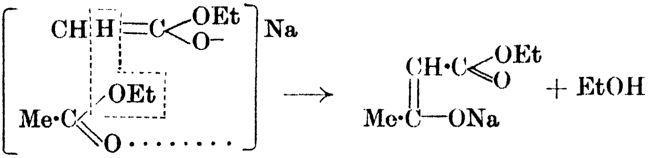
[39] *Ibid.*, 1922, **55**, 789; *A.*, 1922, i, 426.

[40] F. Swarts, *Bull. Soc. chim. Belg.*, 1926, **35**, 412; *A.*, 1927, 646.

[41] *Ber.*, 1929, **62**, 1824; *A.*, 1929, 1041.

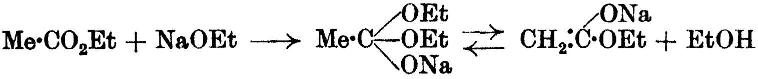
In a reinvestigation of Claisen's synthesis of ethyl cinnamate it was found[42] to be immaterial whether the formation of the sodio-enolate of ethyl acetate was allowed to proceed to completion by keeping for 24 hours before addition of the benzaldehyde, or whether the two reactants were merely added to finely divided sodium in ether. Since the formation of the "primary reaction product" was presumably complete in the first case, this product reacted as if it still contained the enolate (I) and it was therefore formulated as a species of molecular compound; it cannot, of course, be ethyl sodioacetoacetate, because the latter does not react with benzaldehyde in the same way. Subsequently, by analogy with the quinhydrones, it was given the constitution (III), in which the components were assumed to retain their individuality to some extent:[43]

(III.)



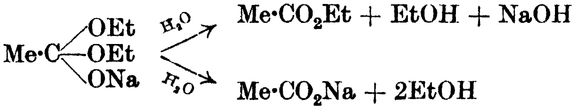
The compound loses alcohol (as shown by the dotted line) on heating, giving ethyl sodioacetoacetate, which no longer gives keten acetal on fission.

Scheibler and Friese[42] found that the elimination of the alcohol formed in the reaction of benzaldehyde with ethyl acetate not only raises the yield of ethyl cinnamate (compare p. 198) but reduces the amount of acetic acid formed as a by-product. They attributed the formation of the latter to the following process:



$$\mathrm{Me{\cdot}CO_2Et + NaOEt \longrightarrow Me{\cdot}C(OEt)_2(ONa) \rightleftarrows CH_2{:}C(ONa){\cdot}OEt + EtOH}$$

(IV.)



$$\mathrm{Me{\cdot}C(OEt)_2(ONa)} \begin{cases} \xrightarrow{H_2O} \mathrm{Me{\cdot}CO_2Et + EtOH + NaOH} \\ \xrightarrow{H_2O} \mathrm{Me{\cdot}CO_2Na + 2EtOH} \end{cases}$$

It was suggested[43] that, in the reaction with benzaldehyde, the latter takes the place of the ketonic molecule of ethyl acetate and the condensation then proceeds as before.

Scheibler's reaction scheme has given rise to much criticism and controversy, an account of which would be beyond the scope of this Report; the following points may, however, be noted. F. Adickes[44] has studied the addition of sodium ethoxide to a variety of esters and found that only a few—formates, oxalates, trifluoroacetates, and a few α-ketonic esters—are capable of forming addition products. He doubts the existence of such esters as (IV) and prefers to regard the formation of the enolate (I) as taking place directly from sodium ethoxide and ethyl acetate; the existence of the ester (II) is also questioned, but this is no longer postulated in Scheibler's latest scheme. Adickes[45] further criticises the mode of elimination of alcohol from the complex (III) (p. 201) as being unnatural; Scheibler[46] is, however, willing to admit an intermediate stage in this process, namely,

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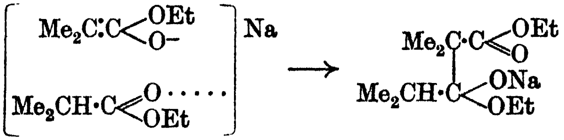
[42] H. Scheibler and H. Friese, *Annalen*, 1925, **445**, 141; *A.*, 1925, i, 1417.

[43] H. Scheibler and E. Marhenkel, *ibid.*, 1927, **458**, 1; H. Scheibler, E. Marhenkel, and R. Nikolić, *ibid.*, p. 21; *A.*, 1927, 1167.

$$\mathrm{Me{\cdot}C(ONa)(OEt){\cdot}CH_2{\cdot}CO_2Et},$$

from which alcohol can be eliminated in a normal manner. The formation of this compound would in effect amount to the addition of the components $\mathrm{Na^+}$ and $\mathrm{CH_2{:}C(OEt){\cdot}O^-}$ to a molecule of the ketonic form of ethyl acetate.

M. C. Franklin and W. F. Short[47] have alkylated the "primary reaction product" and obtained the products to be expected if the latter consisted solely of ethyl sodioacetoacetate; this, as rightly pointed out by Adickes,[45] hardly amounts to proof, because the reaction takes place on heating; and the formation of products presumably derived from an ortho-ester has been reported.[42] They also suggest that if a "primary condensation product" is formed from ethyl *iso*butyrate as claimed by Scheibler and Friese,[42] this should on acidification yield the ketonic ester:



$$\left[\begin{array}{l}\mathrm{Me_2C{:}C{<}^{OEt}_{O^-}}\\ \mathrm{Me_2CH{\cdot}C{\leqslant}^{O\cdots\cdots}_{OEt}}\end{array}\right]\mathrm{Na}\longrightarrow\begin{array}{l}\mathrm{Me_2C{\cdot}C{\leqslant}^{OEt}_{O}}\\ \quad\ \ |\\ \mathrm{Me_2CH{\cdot}C{<}^{ONa}_{OEt}}\end{array}$$

The same point is also raised by S. M. McElvain,[48] who could not substantiate the elimination of alcohol in the reaction between sodium ethoxide and ethyl *iso*butyrate, as would be expected if the initial condensation, depending on the formation of the enolate from the ester, took place, although the elimination of a *second* molecule of alcohol is clearly impossible.

H. Scheibler[46] attributes the poor yield of condensation product from ethyl *iso*butyrate to its low reactivity with sodium ethoxide, and an enolate has, indeed, been prepared from it by the agency of sodium triphenylmethyl :[49] there are, however, disubstituted acetic esters, such as the diethoxy- and diphenoxy-compounds, which react normally with sodium ethoxide;[50] the formation of condensation products can be recognised by their fission to keten acetals. Scheibler regards the formation of the latter as proof of the existence of the primary addition product. The production of these acetals could be repeated neither by A. E. Arbusow[51] nor by J. M. Snell and S. M. McElvain;[52] it has also been suggested that they might be formed as the result of a side reaction.[53]

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[44] *Ber.*, 1925, **58**, 1992; *A.*, 1925, i, 1378; *ibid.*, 1926, **59**, 2522; *A.*, 1927, 41; *ibid.*, 1927, **60**, 272; *A.*, 1927, 227; F. Adickes, W. Brunnert, O. Lücker, and H. Schäfer, *J. pr. Chem.*, 1932, **133**, 305; *A.*, 1932, 614.

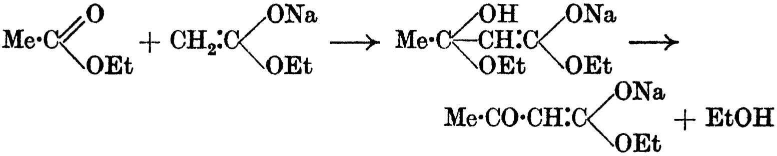
[45] *Ber.*, 1932, **65**, 522; *A.*, 1932, 599.

[46] *Ibid.*, p. 994; *A.*, 1932, 831.

[47] *J.*, 1928, 591; *A.*, 1928, 505.

[48] *J. Amer. Chem. Soc.*, 1929, **51**, 3124; *A.*, 1929, 1424.

G. W. Tschelinzew[53] has lately proposed the following scheme :



This formulation appears to be a natural one, being akin to the aldol reaction and the addition of sodio-esters to ethylene oxide.[54] The latter does not take place with substituted malonic and acetoacetic esters, because no hydrogen is available in their enolates for addition to the ethylene oxide with opening of the ring.

The formation of the enolate of ethyl acetate is formulated as a direct process, as assumed by Adickes, without the formation of an intermediate ortho-ester; the alcohol acts catalytically by forming sodium ethoxide.

Tschelinzew claims that his scheme combines the advantages of Claisen's, which was built round the necessity for a trace of alcohol to start the reaction, and Scheibler's, which was devised to explain the formation of keten acetals. The latter is pictured as a secondary process.

K. Bodendorf[55] has pointed out that the separation of a hydrogen atom from an enolate, which is the first step in Tschelinzew's process, is unlikely, especially as the presence of the metal would tend to strengthen the bond in question; and evidence has lately been adduced to show that it is the metal, and not the hydrogen, which separates in the addition of enolates to unsaturated compounds.[56] Bodendorf suggests that a molecular compound is first formed, the orientation being due to the polarity of the groups involved; the scheme does not appear to differ materially from that of Scheibler.

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[49] H. Scheibler and H. Stein, *Ber.*, 1933, **66**, [*B*], 1784; *A.*, 169.

[50] H. Scheibler, W. Beiser, and W. Krabbe, *J. pr. Chem.*, 1932, **133**, 131; *A.*, 1932, 363.

[51] *Ibid.*, 1931, **64**, [*B*], 698; *A.*, 1931, 599.

[52] *J. Amer. Chem. Soc.*, 1933, **55**, 416, 427; *A.*, 1933, 258, 259; contrast H. Scheibler, *ibid.*, p. 425; *Ber.*, 1933, **66**, [*B*], 428; *A.*, 1933, 259, 377.

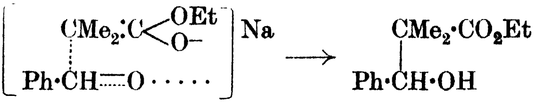
[53] G. W. Tschelinzew, *Ber.*, 1934, **67**, [*B*], 955; *A.*, 868.

[54] W. Traube and E. Lehmann, *Ber.*, 1899, **32**, 720; 1901, **34**, 1971; *A.*, 1899, i, 417; 1901, i, 501; A. Haller, *Compt. rend.*, 1901, **132**, 1459; *A.*, 1901, i, 538.

[55] *Ber.*, 1934, **67**, [*B*], 1338; *A.*, 991.

The inability of disubstituted esters to undergo the reaction is admittedly no longer clearly accounted for and is attributed to the " screening effect " of the additional alkyl groups; the necessary pre-requisite for the first phase of the condensation is a polarisable double bond; in the case of enolisable carbonyl groups, the action of the catalyst consists in the activation of the change ketone -> enol and the displacement of the equilibrium towards the latter.

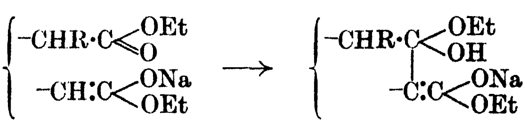
H. Scheibler [57] also criticises Tschelinzew's scheme; he points out that, although ethyl *iso*butyrate does not undergo the ordinary Claisen reaction, it can be condensed with benzaldehyde (p. 201):



$$\left[\begin{array}{l}\mathrm{CMe_2{:}C{<}^{OEt}_{O^-}}\\ \vdots\\ \mathrm{Ph{\cdot}CH{=}O\cdots\cdots}\end{array}\right]\mathrm{Na}\longrightarrow\begin{array}{l}\mathrm{CMe_2{\cdot}CO_2Et}\\ \quad|\\ \mathrm{Ph{\cdot}CH{\cdot}OH}\end{array}$$

A second molecule of ethyl *iso*butyrate cannot take the place of the benzaldehyde in the above scheme, because the resulting compound is incapable of forming an enolate.

When Tschelinzew's scheme is applied to intramolecular acetoacetic (Dieckmann) condensations, the ester group which enolises must be attached to an unsubstituted methylene group:



$$\left\{\begin{array}{l}\mathrm{-CHR{\cdot}C{<}^{OEt}_{O}}\\ \mathrm{-CH{:}C{<}^{ONa}_{OEt}}\end{array}\right.\longrightarrow\left\{\begin{array}{l}\mathrm{-CHR{\cdot}C{<}^{OEt}_{OH}}\\ \qquad\ \ |\\ \mathrm{\ \ -C{:}C{<}^{ONa}_{OEt}}\end{array}\right.$$

The same must, of course, apply when the group R is carbethoxyl. A difficulty now arises, because some esters of this type undergo the Dieckmann reaction even if the α-carbon atom of the acetic chain is substituted, as in the ester (V); [58] this point has been reinvestigated and confirmed [59] and it has been found that this

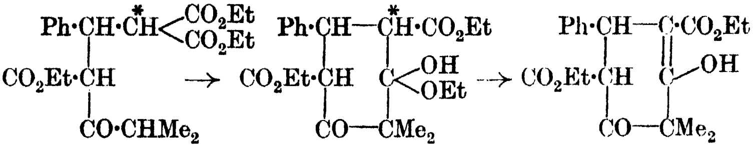
[56] B. S. Gidvani, G. A. R. Kon, and C. R. Wright, *J.*, 1932, 1027; *A.*, 1932, 601.

[57] *Ber.*, 1934, **67**, [*B*], 1341; *A.*, 991.

[58] W. Dieckmann and A. Kron, *ibid.*, 1908, **41**, 1260; *A.*, 1908, i, 388.

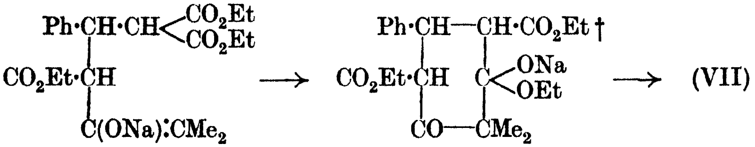
[59] R. F. B. Cox, E. H. Kroeker, and S. M. McElvain, *J. Amer. Chem. Soc.*, 1934, **56**, 1173; R. F. B. Cox and S. M. McElvain, *ibid.*, p. 2459; *A.*, 1934, 756; 1935, 83.

reaction only takes place if the carbethoxyl, which becomes the keto-group of the new ketonic ester, is part of a malonic ester group. McElvain explains these results by Michael's well-known formulation, with the additional assumption that the second hydrogen atom required for the elimination of alcohol from the intermediate compound (VI) is supplied, not by the carbon atom corresponding to the α-carbon in acetoacetic ester, but by the γ-carbon*; this is made possible by the additional activation due to the remaining carbethoxyl group attached to it :



(V.) (VI.) (VII.)

It appears impossible to formulate the cyclisation process with the aid of Tschelinzew's scheme, which differs from Michael's essentially in that the *first* atom of hydrogen taking part in the reaction is supplied by the enolate, not by the ester itself; the enolate of (V) has no hydrogen available for this. In Scheibler's latest scheme the sodium would wander, so that the intermediate compound would have the structure (VIII) :



(VIII.)

For the present the conclusion must inevitably be reached that all the mechanisms put forward to explain the Claisen and related reactions have their weaknesses; more particularly, it appears difficult to reconcile the inability of *iso*butyric ester to condense to a ketonic ester, with the cyclisation of such esters as (V).

These difficulties largely disappear when the Claisen reaction is viewed from the standpoint of the electronic mechanism of organic reactions as developed by Lapworth, Robinson, and Ingold. The existence of the highly reactive sodium enolate of ethyl acetate has been proved by Scheibler, and this, even if present in small amount, would give rise to the ions $\mathrm{Na^+}$ and $\overset{\delta-}{\mathrm{C}}\mathrm{H_2{:}C(OEt){\cdot}O^-}$: the second

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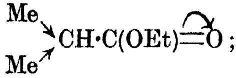
† The above formulation of the enolate is somewhat unusual, but it is necessary to account for the formation of a six-membered ring on cyclisation.

component is a molecule of the ester in the keto-form, $\mathrm{Me\cdot\overset{\delta+}{C}(OEt){=}O}$. Addition follows with the formation of the product

$$\mathrm{Me\cdot C(OEt)(O^-)\cdot CH_2\cdot CO_2Et},$$

the negative charge appearing on the oxygen of the ketonic fragment; this would lead to the formation of Scheibler's enolate, $\mathrm{Me\cdot C(ONa)(OEt)\cdot CH_2\cdot CO_2Et}$, which can then lose alcohol (p. 202).

Taking now the case of ethyl *iso*butyrate, it is clear that the two methyl groups must exercise their usual inductive effect and thus oppose the development of the fractional positive charge in the ketonic component:



$$\mathrm{\begin{matrix}Me\searrow\\Me\nearrow\end{matrix}CH\cdot C(OEt){=}O}$$

; at the same time, an accumulation of electron-donating groups is clearly unfavourable to the removal of a proton in the formation of an enolate, which is produced by a reversible process, $\mathrm{Me_2CH\cdot CO_2Et + NaOEt \rightleftharpoons Me_2C{:}C(OEt)\cdot ONa + EtOH}$, although this compound can be obtained in the presence of triphenylmethyl, a weaker acid than alcohol. The condensation with benzaldehyde would indicate that the enolate is formed to some extent even in the presence of alcohol. The ready condensation of ethyl diethoxyacetate is to be explained by the fact that the inductive effect of the ethoxyl group, though feeble, is in the opposite sense to that of the methyl group $(-I)$; it also has a strong electromeric effect $(+T)$, but this is not called into play in the present example, the reaction requiring a recession of electrons. In other words, the Claisen reaction is inhibited, not by the introduction of two substituents into ethyl acetate, but by their nature. The condensation studied by Dieckmann and Kron (p. 204) can also be easily explained.

The necessity for a trace of alcohol to induce the Claisen reaction lends strong support to the view that the active agent is the enolate ion $\mathrm{CH_2{:}C(OEt)\cdot O^-}$, which is formed by the dissociation of the enolate in the presence of alcohol.

Animal and Vegetable Hormones.

Although the substances dealt with in this section belong to two widely different types, it is convenient to consider them together because they provide an instructive contrast.

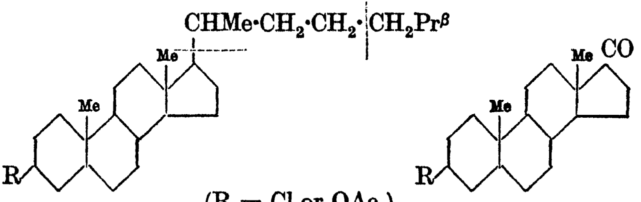
The elucidation of the structure of the auxins, compounds containing 18 carbon atoms, carried out with less than a gram of material, can justly be hailed as an outstanding triumph of the analytical method of investigation. The identity of an oxidation product of epicholestanol with the male sexual hormone (androsterone) establishes the constitution of the latter in spite of the fact that the amount of the pure product isolated from natural sources barely sufficed for the determination of its empirical formula; the method of investigation employed in this case is essentially synthetic, even though it cannot be described as a synthesis in the strict sense of the word because the starting material was a natural product. The structure of the active principle of the *corpus luteum* of animals also was ascertained by a synthetic method: the starting material (stigmasterol) in this case belongs to the vegetable, not the animal, kingdom.

Androsterone.—As already noted, the male sexual hormone, androsterone, has been isolated in minute quantities, sufficient to establish its formula, $C_{19}H_{30}O_2$, and its character as a hydroxy-ketone.[60] Its sterol-like structure and the relationship to œstrone, from which it differs by being fully saturated, were merely surmised, although it has been found that an amorphous octahydro-derivative of œstrone has a similar, if less pronounced, physiological activity.[61]

Androsterone gives on oxidation [62] a diketone reducible by Clemmensen's method to the saturated hydrocarbon, androstane, which is not identical with ætiocholane; and similarly, androstanone, in which the hydroxyl group of androsterone is replaced by hydrogen, is not identical with ætiocholanone, the final product obtained by the degradation of the side chain of the bile acids. This shows that, stereochemically, androsterone does not belong to the bile acid (cholane) series.

L. Ruzicka, M. W. Goldberg, and H. Brüngger [63] have found that β-cholestanyl chloride and cholestanyl acetate could be oxidised by chromic acid to ketones (in addition to the corresponding cholanic acids) in which the side chain is completely removed; the two points of attack are indicated by dotted lines:

(I.)



(II.)

(R = Cl or OAc.)

This reaction had already been used [64] to ascertain the nature of the side chain in cholesterol, but only the volatile product, methyl *iso*hexyl ketone, was isolated.

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[60] A. Butenandt, *Naturwiss.*, 1933, **21**, 54; *A.*, 1933, 322; A. Butenandt and K. Tscherning, *Z. physiol. Chem.*, 1934, **229**, 167, 185.

[61] W. Schoeller, E. Schwenk, and F. Hildebrandt, *Naturwiss.*, 1933, **21**, 286; *A.*, 1933, 755; compare W. Dirscherl and H. E. Voss, *ibid.*, p. 315; contrast A. Girard, *Bull. Soc. Chim. biol.*, 1933, **15**, 601; *A.*, 1933, 870.

[62] A. Butenandt and H. Dannenbaum, *Z. physiol. Chem.*, 1934, **229**, 192.

[63] *Helv. Chim. Acta*, 1934, **17**, 1387; *A.*, 1221.

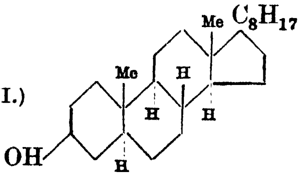
[64] A. Windaus and C. Resau, *Ber.*, 1913, **46**, 1246; *A.*, 1913, i, 615.

Both the chloro-compound and the corresponding alcohol, 3-hydroxyaetio*allo*cholan-17-one, showed a distinct physiological activity, as measured by the growth of the comb in capons, following their administration.

In a later paper [65] the oxidation of the three remaining isomerides of cholestanyl acetate is described. The preparation of the requisite alcohols (cholestanol, coprostanol, and their epimerides) [*] was reinvestigated and greatly improved; [66] it was found that the catalytic reduction of coprostanone (the latter in turn obtained by the reduction of coprostenone) with platinum in acid solution gave coprostanol, whereas in neutral solution the epimeride was formed; this is no longer precipitated by digitonin and is also formed from coprostanol by the action of sodium alkoxides at 180°.

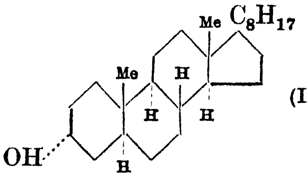
Cholestanone in the same way yielded cholestanol and epicholestanol, of which only the former is precipitated by digitonin, but here the epi-compound was formed in acid solution and was converted into cholestanol by sodium alkoxides. The four alcohols are given the following configurations :

(III.)



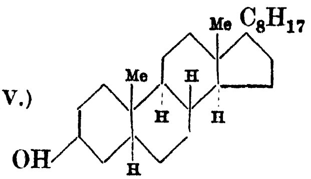
Cholestanol.
trans, trans, trans, trans.

(IV.)



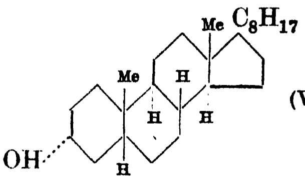
Epicholestanol.
cis, trans, trans, trans.

(V.)



Coprostanol.
cis, cis, trans, trans.

(VI.)



Epicoprostanol.
trans, cis, trans, trans.

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[65] L. Ruzicka, M. W. Goldberg, J. Meyer, H. Brüngger, and E. Eichenberger, *Ber.*, 1913, **46**, 1395; *A.*, 1221.

[66] L. Ruzicka, H. Brüngger, E. Eichenberger, and J. Meyer, *Helv. Chim. Acta*, 1934, **17**, 1407; *A.*, 1221; G. Vavon and B. Jakubowicz, *Bull. Soc. chim.*, 1933, **53**, 584; *A.*, 1933, 1047.

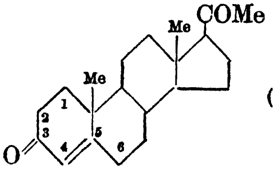
[*] The nomenclature is that of O. Rosenheim and H. King, *Chem. and Ind.*, 1934, **53**, 91; *A.*, 292.

The mode of ring fusion is that previously deduced,[67] and the configuration of the hydroxyl relative to the ring follows the Auwers–Skita rule (it is not regarded as final).

Four hydroxyætiocholanones (II, R = OH) have been prepared from these alcohols; of these, that derived from epicholestanol (IV) is identical with Butenandt's androsterone and has the same high degree of biological activity: its epimeride, corresponding to the alcohol (III), also shows some activity, but the two derivatives of coprostanol are apparently inactive. Androsterone is the first compound of the epicholestanol series to be isolated from natural sources.

Corpus Luteum Hormone.—The crystalline hormone has recently been isolated from extracts of *corpora lutea* (for details, see the biochemical section of these Reports) by four groups of workers [68, 69, 70, 71] and characterised as an unsaturated [69] diketone (luteosterone C), $C_{20}H_{30}O_2$, melting at about 128°; it is accompanied, apart from inactive compounds, by an isomeride (luteosterone D), m. p. 121—122°, which is converted into the higher-melting compound when heated.[69] Later work has shown that the two compounds are merely polymorphic varieties of the same structure and activity.[72]

Luteosterone has an absorption spectrum indicating that the double bond is in the αβ-position to one of the keto-groups; the formula (VII) was suggested for it as a working hypothesis and has



(VII.)

since been confirmed by the preparation of the pure hormone in several ways.[73]

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[67] L. Ruzicka, M. Furter, and G. Thomann, *Helv. Chim. Acta*, 1933, **16**, 327; *A.*, 1933, 495; compare *Ann. Reports*, 1933, **30**, 209.

[68] A. Butenandt, U. Westphal, and W. Hohlweg, *Z. physiol. Chem.*, 1934, **227**, 84; *A.*, 1268.

[69] K. H. Slotta, H. Ruschig, and E. Fels, *Ber.*, 1934, **67**, [*B*], 1270; *A.*, 931.

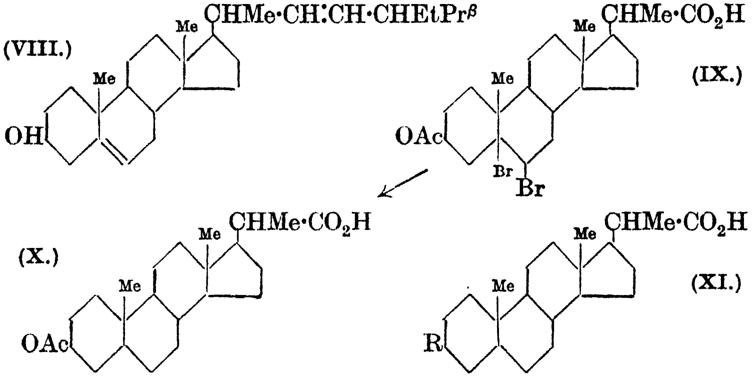
[70] M. Hartmann and A. Wettstein, *Helv. Chim. Acta*, 1934, **17**, 878, 1365; *A.*, 1039, 1412.

[71] W. M. Allen and O. Wintersteiner, *Science*, 1934, **80**, 190; *A.*, 1268.

[72] A. Butenandt and J. Schmidt, *Ber.*, 1934, **67**, [*B*], 2088.

[73] A. Butenandt, U. Westphal, and H. Cobler, *ibid.*, p. 1611; K. H. Slotta, H. Ruschig, and E. Fels, *ibid.*, p. 1624; *A.*, 1268. The former authors also considered the possibility of the double bond being in position C_{5-6}, which was disproved by spectrographic work.

Before these can be discussed, it is necessary to consider the constitution of stigmasterol, a phytosterol occurring in the soya bean. The side chain of this sterol contains a double bond and one carbon atom more than that of ergosterol, as it gives ethyl*iso*propylacetaldehyde on ozonisation.[74] E. Fernholz[75] found that bromine could be added to the other double bond, situated in the nucleus, without affecting the one in the side chain. The acetate of this dibromide was ozonised, a portion of the side chain being removed; the product on debromination was reduced and finally hydrolysed to 3-hydroxy*allo*bisnorcholanic acid (XI; R = OH):



The hydroxyl group was oxidised and the ketonic acid formed was reduced by Clemmensen's method to bis*allo*norcholanic acid (XI; R = H). The same acid was also prepared from *allo*norcholanic[76] acid by shortening of the chain by Wieland's well-known method.[77] This sequence of operations proves that stigmasterol contains the same ring system as cholesterol and ergosterol.

The next step was the proof that the hydroxyl group and the double bond are in the same relative position ($\gamma\delta$) as in cholesterol. This was achieved[78] by the procedure already employed for the latter sterol,[79] and led to the isolation of the diketone stigmastenedione (XII); this was proved to be a γ-diketone by the formation of a cyclic compound (XIII) with hydrazine:

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[74] See *Ann. Reports*, 1933, **30**, 211.

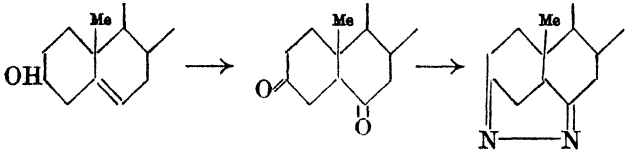
[75] *Annalen*, 1933, **507**, 128; *A.*, 1933, 1290.

[76] C. K. Chuang, *ibid.*, 1933, **500**, 270; *A.*, 1933, 391.

[77] H. Wieland, O. Schlichting, and R. Jacobi, *Z. physiol. Chem.*, 1926, **161**, 80; *A.*, 1927, 247.

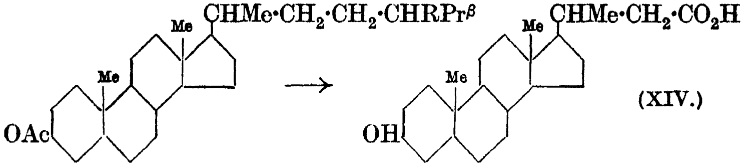
[78] *Idem, ibid.*, 1934, **508**, 215; *A.*, 293.

[79] A. Windaus and E. Kirchner, *Ber.*, 1920, **53**, 614; *A.*, 1920, i, 425; *Ann. Reports*, 1927, **24**, 133.



(XII.) (XIII.)

The position of the hydroxyl on C_3 in stigmasterol and also in ergosterol was later established by E. Fernholz and P. N. Chakravorty;[80] this constitutes an important advance in our knowledge. The acetates of stigmastanol and ergostanol, the saturated alcohols corresponding to these two sterols, were subjected to oxidation with chromic acid by the method already employed by Ruzicka and his collaborators[64, 65] in the cholestanol series. The main acid product, after hydrolysis, was the same β-3-hydroxy*allo*norcholanic acid (XIV):

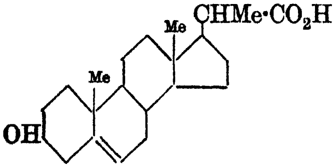


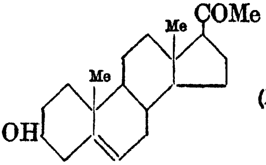
R = Me in ergostanol, and Et in stigmastanol.

Cholestanol gave under the same conditions β-3-hydroxy*allo*cholanic acid, and this gave, on shortening of the chain by Wieland's method, an acid identical with (XIV). This leads to the important conclusion that not only is the hydroxyl group in the same position in all three sterols, but the stereochemical arrangement is the same.

A mixture of compounds having a physiological activity approaching that of luteosterone C was prepared[81] from Fernholz's 3-hydroxybisnorcholenic acid (XV); the ester of this, on shortening of the chain by Wieland's process, gave the hydroxy-ketone (XVI), and this was oxidised under mild conditions.

(XV.)





(XVI.)

The pure diketone (VII) was then obtained independently by E. Fernholz[82] and by Butenandt and his collaborators. Fernholz oxidised the dibromide of the hydroxy-ketone (XVI) with acid permanganate; on removal of the bromine from the diketone (XVII), luteosterone was obtained. In a later paper [83] he describes the direct oxidation of the hydroxy-ketone with copper oxide.

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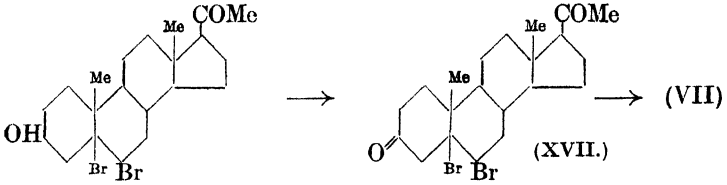
[80] *Ber.*, 1934, **67**, [*B*], 2021.

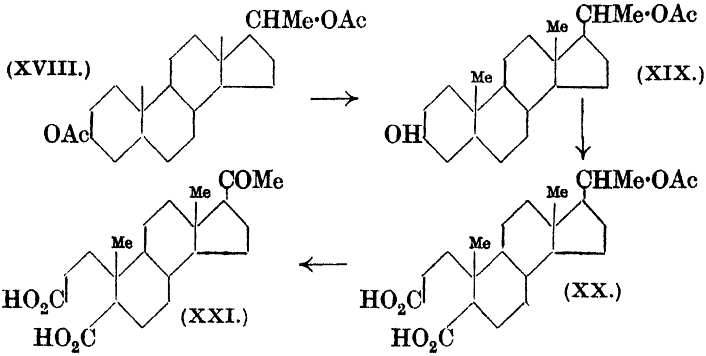
[81] A. Butenandt, U. Westphal, and H. Cobler, *ibid.*, p. 1611; *A.*, 1268.

[82] *Ibid.*, p. 1855; *A.*, 1935, 128.


(XVII.)

The position of the double bond follows by analogy with coprostenone (cholestenone),[84] which is formed in a similar manner.

A. Butenandt and J. Schmidt [85] also carried out the sequence of operations described above and, in addition, prepared luteosterone from pregnanediol, the constitution of which had already been settled.[86] Butenandt and Schmidt[87] found that the diacetate of pregnanediol (XVIII) could be partly hydrolysed to the monoacetate (XIX). The constitution of this follows from its oxidation with chromic acid to a dibasic acid (XX), ring I being opened; the acid, on deacetylation and oxidation of the hydroxyl, passes into the ketonic acid (XXI) already obtained from pregnanediol.


(XVIII.) (XIX.) (XX.) (XXI.)

The monoacetate can be oxidised to the acetate of pregnanol-3-one (XXII), which is physiologically inactive.

On bromination,[85] this ketone gives a bromo-ketone, which is oxidised to the bromo-diketone (XXIII); the latter can also be obtained by the direct bromination of pregnanedione. The unsaturated diketone obtained on removal of the bromine occurs in two forms, identical with the two forms of luteosterone (C and D). It is clear that the bromine atom could enter the position 2, on the other side of the keto-group, and this would lead to a ketone with a double bond in the position 1 : 2; this possibility is, however, precluded by the alternative preparation from stigmasterol, which must lead to a double bond at either $C_{4:5}$ or $C_{5:6}$. In the former case it is necessary to assume the wandering of the double bond to a position αβ to the keto-group.[88]

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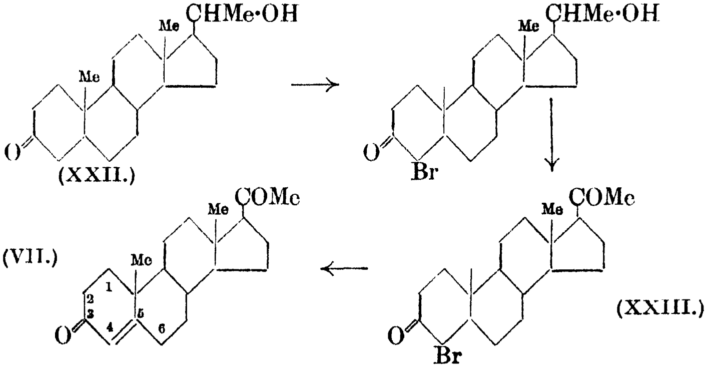
[83] *Ber.*, 1934, **67**, [*B*], 2027.

[84] K. Bonstedt, *Z. physiol. Chem.*, 1933, **214**, 173; *A.*, 1933, 390.

[85] *Ber.*, 1934, **67**, [*B*], 1901.

[86] A. Butenandt, *ibid.*, 1931, **64**, 2529; *A.*, 1932, 54.

[87] *Ibid.*, 1934, **67**, [*B*], 1893.

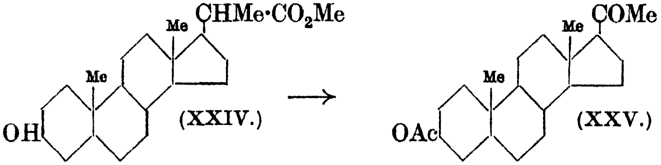


(XXII.)

(VII.)

(XXIII.)

The structure of a physiologically inert, saturated hydroxy-ketone, which accompanies luteosterone, has also been settled.[89] The diketone obtained from it by oxidation was not identical with pregnanedione, the difference being attributed to stereoisomerism. This was confirmed as follows: the methyl ester of Fernholz's 3-hydroxy*allo*bisnorcholanic acid (p. 210) was subjected to degradation by Wieland's method; the acetate of a hydroxy-ketone (XXV) was then obtained, which on hydrolysis yielded *allo*pregnanol-20-one, identical with the inactive ketone found in *corpus luteum* extracts.



(XXIV.)

(XXV.)

This compound therefore belongs to the cholestane series, whereas pregnanediol is a coprostane derivative. Now the hormone itself has a double bond adjoining the point of fusion of the two rings; it can therefore give rise to both cholestane and coprostane derivatives on reduction according to the mode of addition of the hydrogen to C_5. For this reason it is suggested that *allo*pregnanol-20-one and pregnanediol are probably two of the several possible reduction products of the hormone.

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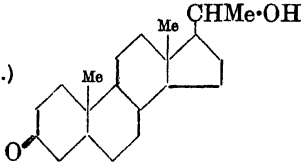
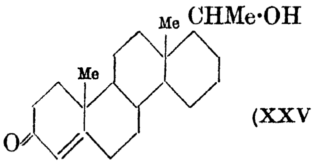
[88] Compare A. Butenandt and U. Westphal, *Ber.*, 1934, **67**, [*B*], 2085.

[89] A. Butenandt and L. Mamoli, *ibid.*, p. 1897.

The hydroxy-ketone (XXVI), obtained by brominating the ketone (XXII) and removing the bromine[90] without previous oxidation to the diketone (p. 212), is devoid of physiological activity, thus illustrating the specific character of the hormone.

(XXII.)

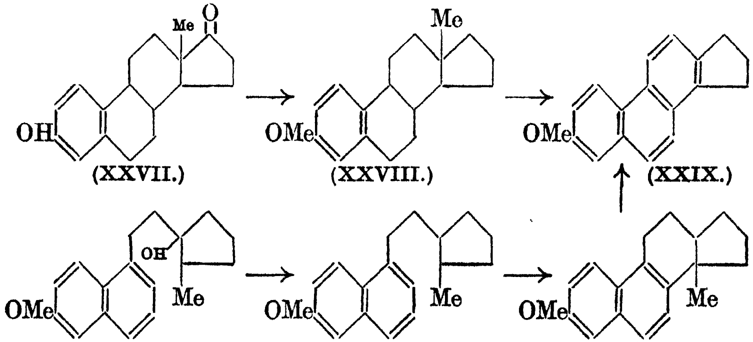




(XXVI.)

Œstrone and Equilenin.—An important development in the investigation of these substances is the determination of the position of the phenolic hydroxyl group; the experiments also provide the final proof of the type of ring structure, which had hitherto been assumed.

Œstrone (XXVII) was methylated, the keto-group reduced, and the desoxo-compound (XXVIII) dehydrogenated with selenium to the methoxy-hydrocarbon (XXIX).[91] The identity of the latter was established by synthesis by the steps indicated:[92]



(XXVII.) (XXVIII.) (XXIX.) (XXX.)

The methyl ether of equilenin[93] can be converted into a desoxo-compound, which is dehydrogenated to the same aromatic compound (XXIX). Desoxoequilenin must have the structure (XXXI) and is not identical with the compound (XXX) obtained in the course of the synthesis of (XXIX); but, as the authors rightly point out, this does not definitely establish the position of the methyl group in equilenin, because both desoxo-compounds can exist in two stereoisomeric forms (both resolvable).

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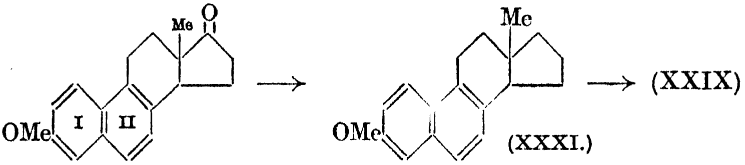
[90] A. Butenandt and J. Schmidt, *Ber.*, 1934, **67**, [*B*], 2092.

[91] J. W. Cook and A. Girard, *Nature*, 1934, **133**, 377; *A.*, 404.

[92] A. Cohen, J. W. Cook, C. L. Hewett, and A. Girard, *J.*, 1934, 653; *A.*, 766.

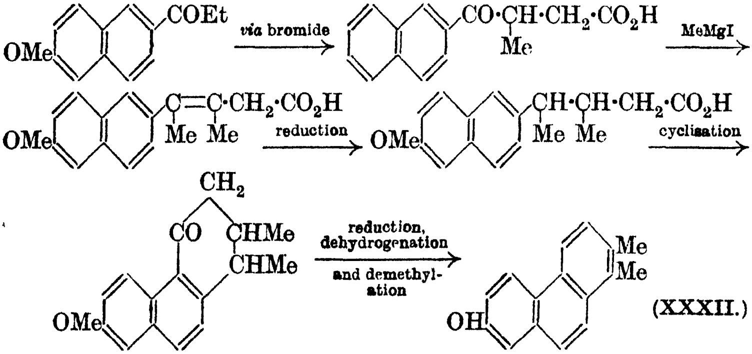
[93] See *Ann. Reports*, 1933, **30**, 342.



(XXXI.) → (XXIX)

From these results it follows that œstrone and equilenin contain the ring system of *cyclo*pentenophenanthrene and therefore belong to the sterol group. The phenolic hydroxyl of œstrone is situated in ring I, which is therefore the aromatic ring in this substance; as equilenin contains a naphthalene ring system, it follows that in this compound the second benzenoid ring is II.

Almost simultaneously with Cook and his collaborators, R. D. Haworth and G. Sheldrick [94] described the synthesis of 7-hydroxy-1 : 2-dimethylphenanthrene (XXXII), which was found to be identical with the phenolic product of the degradation of œstrone.[95] The synthesis was carried out as follows:



(XXXII.)

There remains, therefore, only to establish the positions of the keto-group and the quaternary methyl in these compounds.

Auxins (continued from *Ann. Reports*, 1933, **30**, 195). It has already been pointed out that the final elucidation of the structure of auxins *a* and *b* is contingent on the identification of an optically active dibasic acid, $C_{13}H_{24}O_4$, probably a glutaric acid, obtained from these compounds on oxidation. This has now been achieved in spite of the fact that the amount of C_{13} acid employed was only 90 mg.[96] The acid (XXXIII) was dibrominated and then treated with silver oxide, the silver salt of the dihydroxy-acid (XXXIV) converted into the methyl ester with the aid of methyl iodide, and this treated with methylmagnesium iodide. The glycol formed was treated with lead tetra-acetate,[97] a colourless, optically active β-diketone (XXXVIII) being obtained :

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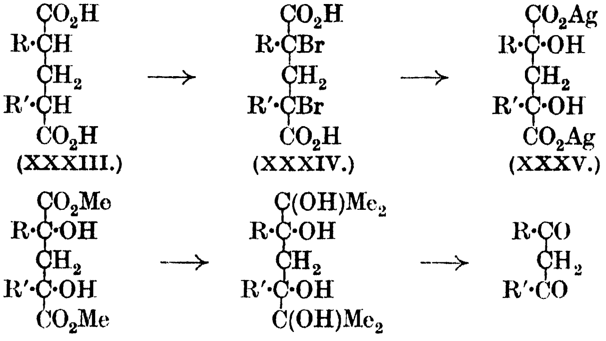
[94] *J.*, 1934, 864; *Chem. and Ind.*, 1934, **53**, 431; *A.*, 885, 767.

[95] A. Butenandt, H. A. Weidlich, and H. Thompson, *Chem. and Ind.*, 1933, **52**, 268; *Ber.*, 1933, **66**, [*B*], 601; *A.*, 540; compare *Ann. Reports*, 1933, **30**, 216.



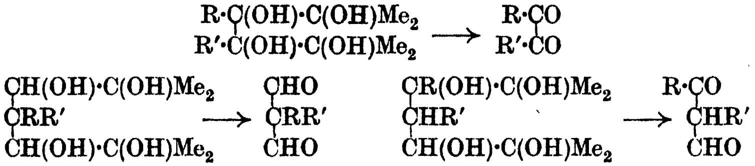
$$\begin{array}{c}CO_2H\\R\cdot CH\\CH_2\\R'\cdot CH\\CO_2H\end{array}\longrightarrow\begin{array}{c}CO_2H\\R\cdot CBr\\CH_2\\R'\cdot CBr\\CO_2H\end{array}\longrightarrow\begin{array}{c}CO_2Ag\\R\cdot C\cdot OH\\CH_2\\R'\cdot C\cdot OH\\CO_2Ag\end{array}$$

(XXXIII.) (XXXIV.) (XXXV.)

$$\begin{array}{c}CO_2Me\\R\cdot C\cdot OH\\CH_2\\R'\cdot C\cdot OH\\CO_2Me\end{array}\longrightarrow\begin{array}{c}C(OH)Me_2\\R\cdot C\cdot OH\\CH_2\\R'\cdot C\cdot OH\\C(OH)Me_2\end{array}\longrightarrow\begin{array}{c}R\cdot CO\\CH_2\\R'\cdot CO\end{array}$$

(XXXVI.) (XXXVII.) (XXXVIII.)

A β-diketone could not have been produced from an acid of the succinic series, as this would lead to an α-diketone, or from a ββ-disubstituted glutaric acid, which would yield a dialkylated (and therefore not enolisable) malondialdehyde. An αβ-disubstituted glutaric acid would similarly give rise to a hydroxymethylene ketone :



$$\begin{array}{c}R\cdot C(OH)\cdot C(OH)Me_2\\R'\cdot C(OH)\cdot C(OH)Me_2\end{array}\longrightarrow\begin{array}{c}R\cdot CO\\R'\cdot CO\end{array}$$

$$\begin{array}{l}CH(OH)\cdot C(OH)Me_2\\CRR'\\CH(OH)\cdot C(OH)Me_2\end{array}\longrightarrow\begin{array}{c}CHO\\CRR'\\CHO\end{array}\qquad\begin{array}{l}CR(OH)\cdot C(OH)Me_2\\CHR'\\CH(OH)\cdot C(OH)Me_2\end{array}\longrightarrow\begin{array}{c}R\cdot CO\\CHR'\\CHO\end{array}$$

A differentiation between the last type of compound and a true β-diketone was possible because the product from auxin was only moderately acidic.

The diketone was subjected to alkaline hydrolysis and gave dextrorotatory α-methylbutyric acid, and methyl *sec.*-butyl ketone, which was inactive doubtless owing to racemisation. These products being homogeneous, the parent diketone must be symmetrical; otherwise fission in two directions would be anticipated :

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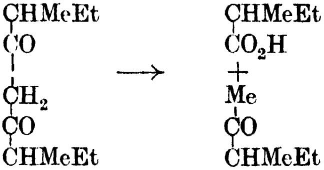
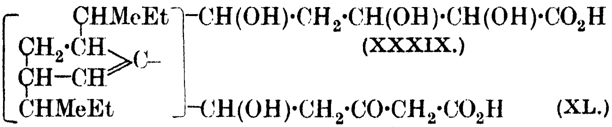
[96] F. Kögl and H. Erxleben, *Z. physiol. Chem.*, 1934, **227**, 51; *A.*, 1332.

[97] R. Criegee, *Ber.*, 1931, **64**, 260; *A.*, 1931, 461; *Annalen*, 1932, **495**, 211; *A.*, 1932, 722; R. Criegee, L. Kraft, and B. Rank, *ibid.*, 1933, **507**, 159; *A.*, 1933, 1272; P. Karrer, F. Benz, R. Morf, H. Raudnitz, M. Stoll, and T. Takahashi, *Helv. Chim. Acta*, 1932, **15**, 1399; *A.*, 1933, 52.



$$\begin{array}{c} \mathrm{CHMeEt} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CHMeEt} \end{array} \longrightarrow \begin{array}{c} \mathrm{CHMeEt} \\ | \\ \mathrm{CO_2H} \\ + \\ \mathrm{Me} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CHMeEt} \end{array}$$

The C_{13} acid is therefore αα′-di-*sec.*-butylglutaric acid; hence the formulæ of auxin *a* and *b* are, respectively, (XXXIX) and (XL) :

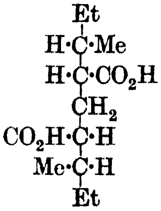


(XXXIX.)

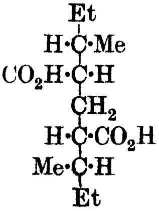
(XL.)

When the acetal of auxin *b* was oxidised with permanganate, there was formed, in addition to the C_{13} acid, *cis*-glutaconic acid; this is clearly derived from the end of the chain carrying the carboxyl. It could, of course, be formed from a γ- or a δ-ketonic acid, but the elimination of carbon dioxide on melting would then be difficult to understand.

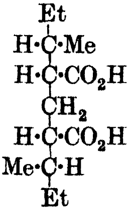
The oxidation of auxin *a* with lead tetra-acetate gives glyoxylic acid and a C_{16} acid, thus further confirming the correctness of the formula (XXXIX) assigned to auxin *a*. The only point still awaiting elucidation is the exact configuration of the groups in the C_{13} acid, and this will no doubt be settled by synthesis. The number of possibilities has already been diminished, for, if the configuration of the two similar groups on the α-carbons were different, the diketone (XXXVIII) would be internally compensated and would give an inactive α-methylbutyric acid. For this reason the following configurations are regarded as possible, all representing resolvable forms of the C_{13} acid :



$$\begin{array}{c} \mathrm{Et} \\ \mathrm{H{\cdot}C{\cdot}Me} \\ \mathrm{H{\cdot}C{\cdot}CO_2H} \\ \mathrm{CH_2} \\ \mathrm{CO_2H{\cdot}C{\cdot}H} \\ \mathrm{Me{\cdot}C{\cdot}H} \\ \mathrm{Et} \end{array}$$



$$\begin{array}{c} \mathrm{Et} \\ \mathrm{H{\cdot}C{\cdot}Me} \\ \mathrm{CO_2H{\cdot}C{\cdot}H} \\ \mathrm{CH_2} \\ \mathrm{H{\cdot}C{\cdot}CO_2H} \\ \mathrm{Me{\cdot}C{\cdot}H} \\ \mathrm{Et} \end{array}$$



$$\begin{array}{c} \mathrm{Et} \\ \mathrm{H{\cdot}C{\cdot}Me} \\ \mathrm{H{\cdot}C{\cdot}CO_2H} \\ \mathrm{CH_2} \\ \mathrm{H{\cdot}C{\cdot}CO_2H} \\ \mathrm{Me{\cdot}C{\cdot}H} \\ \mathrm{Et} \end{array}$$

Cardiac Aglucones.

Although substances having a powerful cardiotonic activity have long been known and utilised in medicine, the examination of their chemical nature has but lately yielded definite results; this is due not only to their complexity but also to the difficulty attending the isolation and characterisation of the active principles, which are frequently amorphous, inseparable mixtures of closely related compounds.

The principal sources of cardiac poisons are plants of the order *Apocynaceae*, but they occur also in representatives of other orders; species of *Digitalis* (foxglove) have valuable medicinal properties, and species of *Strophanthus* are prized as sources of arrow poisons. The venom of several species of toad contains constituents apparently closely related to these cardiac poisons.[98]

The active compounds of plant origin are glucosides and a large number of them have been described, especially by Schmiedeberg and later by Kiliani. The seeds of *Digitalis purpurea* contain the water-soluble digitalin, also found in the leaves; the latter yield the alcohol-soluble digitoxin and the sparingly soluble gitoxin;[99] *Digitalis lanata* yields gitoxin and digoxin.[1] The very thorough reinvestigation by A. Stoll and W. Kreis [2] showed that, if elaborate precautions are taken to prevent secondary changes, the glucosides obtained from *Digitalis* are more complex than was originally supposed and can be isolated in a highly crystalline form. The leaves of *D. lanata* contain a mixture of three digilanides (A, B, and C), which form mixed crystals on fractional crystallisation but can be separated by partition between suitable solvents. Digilanide A yields on mild alkaline hydrolysis a molecule of acetic acid and a desacetyl compound apparently identical with the purpurea-glucoside A found by the authors in the leaves of *D. purpurea*. Cleavage of this by the enzyme found in *Digitalis* leaves gives glucose and digitoxin, which on acid hydrolysis yields the desoxy-sugar, digitoxose (3 mols.), and the aglucone, digitoxigenin. The other two digilanides behave in exactly the same way, but give gitoxigenin and digoxigenin respectively. If the digilanide is directly subjected to acid hydrolysis, it gives the aglucone, acetic acid, two mols. of digitoxose, and digilanidobiose (a disaccharide of digitoxose and glucose). The glucosides of squills are similar:[3] scillaren A is hydrolysed by enzymes to glucose and proscillaridin A; the latter requires hydrolysis with acid to remove rhamnose, leaving the aglucone, scillaridin. This can also be obtained directly by the acid hydrolysis of scillaren A, a disaccharide (scillabiose) being split off. A similar relationship had been previously discovered between the different glucosides of *Strophanthus* : [4] K-strophanthin-β from *S. Kombe* seeds gives on treatment with strophanthobiase glucose and cymarin, already isolated from Canadian hemp,[5] further hydrolysed to cymarose and strophanthidin; acid hydrolysis gives strophanthidin and a biose. Jacobs and Hoffmann showed that the sugar is attached to the secondary hydroxyl group of the aglucone.

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[98] For a detailed account, see W. A. Jacobs, *Physiol. Reviews*, 1933, **13**, 222.

[99] A. Windaus and G. Schwarte, *Ber.*, 1925, **58**, 1515; *A.*, 1925, i, 1295.

[1] S. Smith, *J.*, 1930, 509; 1931, 23; *A.*, 1930, 583; 1931, 74.

[2] *Helv. Chim. Acta*, 1933, **16**, 1049; *A.*, 1933, 877.

[3] A. Stoll, E. Suter, W. Kreis, B. B. Bussemaker, and A. Hofmann, *ibid.*, p. 703; *A.*, 1933, 811.

The following aglucones have been definitely characterised :

Strophanthidin	$C_{23}H_{32}O_6$ [6]	Sarmentogenin ...	$C_{23}H_{34}O_5$ [10]
Digitoxigenin	$C_{23}H_{34}O_4$ [7]	Uzarigenin	,, [11]
Gitoxigenin	$C_{23}H_{34}O_5$ [8]	Ouabagenin	$C_{23}H_{34}O_8$ [12]
Digoxigenin	,, [1]	Scillaridin A	$C_{25}H_{32}O_3$ [13]
Periplogenin	,, [9]		

the structure of others, such as antiarigenin, is still uncertain.

With the exception of scillaridin A, which will be dealt with separately, all these substances are related and possess the same skeleton : they are lactones, requiring one equivalent of alkali for hydrolysis, and contain a double bond, which can be catalytically reduced with the formation of saturated dihydro-derivatives. They must therefore embody a system of four carbon rings; the surmise that they are related to the sterols [13] has only lately been experimentally confirmed.

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[4] W. A. Jacobs and A. Hoffmann, *J. Biol. Chem.*, 1926, **69**, 153; 1926, **67**, 609; *A.*, 1926, 982, 618.

[5] A. Windaus and L. Herrmanns, *Ber.*, 1915, **48**, 979, 991; *A.*, 1915, i, 703, 704.

[6] W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, 1922, **54**, 253; *A.*, 1923, i, 123. These authors were the first to recognise the correct empirical formula of the compound.

[7] M. Cloetta, *Arch. Exp. Path. Pharmakol.*, 1920, **88**, 138; *A.*, 1921, i, 39; A. Windaus and C. Freese, *Ber.*, 1925, **58**, 2503; *A.*, 1926, 153. The correct formula of this "genin" was first ascertained by A. Windaus, *Nach. Ges. Wiss. Göttingen*, 1926, 170.

[8] A. Windaus and G. Schwarte, *Ber.*, 1925, **58**, 1515; *A.*, 1925, i, 1295. The C_{23} formula was first suggested by W. A. Jacobs and E. L. Gustus, *J. Biol. Chem.*, 1928, **78**, 573; *A.*, 1928, 1120.

[9] W. A. Jacobs and A. Hoffmann, *ibid.*, 1928, **79**, 519; *A.*, 1928, 1359; E. Lehmann, *Arch. Pharm.*, 1897, **235**, 157; *A.*, 1897, i, 626.

[10] W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, 1929, **81**, 765; *A.*, 1929, 729.

[11] A. Windaus and E. Haack, *Ber.*, 1930, **63**, 1377; *A.*, 1930, 1024.

[12] W. A. Jacobs and N. M. Bigelow, *J. Biol. Chem.*, 1932, **96**, 647; *A.*, 1932, 856.

[13] A. Windaus and G. Bandte, *Ber.*, 1923, **56**, 2001; *A.*, 1923, i, 1007.

The elucidation of their structure is largely due to A. Windaus and especially W. A. Jacobs and his collaborators, who worked principally on strophanthidin. The chemistry of this compound is in many respects typical of that of the whole group and will be reviewed in some detail, although in the space available only the most important reactions can be considered.

Strophanthidin contains, apart from the lactone group, a carbonyl group and forms an oxime;[14] it also has a secondary hydroxyl, which can be acylated, and two other hydroxyls.[15] The carbonyl forms part of an aldehyde group; oxidation with neutral permanganate in acetone gives an acid (strophanthidinic acid) containing one atom of oxygen more than strophanthidin.[16]

The lactone group. This is the most characteristic portion of the molecule; it constitutes a separate side chain of four carbon atoms, which can be removed by oxidation (of trianhydrostrophanthidin; see p. 226), leaving a carboxyl in its place.[17]

The double bond is associated with it and on this connexion depend both the physiological activity and the characteristic colour reactions of strophanthidin (and all the related aglucones) with sodium nitroprusside (Legal reaction) and with Tollens's reagent. These reactions are typical of Δ^{β}-unsaturated lactones, such as the angelicalactones,[18] which have an "active" hydrogen atom as shown by the Zerevitinov test; they are no longer exhibited by the dihydro-derivative, the physiological activity of which is also comparatively feeble.[19]

W. A. Jacobs and A. B. Scott[20] found that lactones of this type undergo fission on reduction, with the exception of those having a substituent on the β-carbon atom.[21] All the cardiac aglucones of this group are reduced without the opening of the lactone ring and it is therefore inferred that the lactone ring must be attached to the main skeleton through its β-carbon atom.

The most striking reaction of the lactone group, and one which supplies the final proof of its structure, is the isomerisation under the influence of alkali, *iso*strophanthidin, also a lactone, being formed. It was at first thought that the lactone ring of *iso*strophanthidin involved a hydroxyl other than that originally concerned,^{5} but the true nature of the change was revealed when it was shown that *iso*strophanthidin is no longer unsaturated.[22] It is now formulated as follows :

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[14] W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, 1922, **54**, 253; *A.*, 1923, i, 123.

[15] W. A. Jacobs and A. M. Collins, *ibid.*, 1924, **59**, 713; *A.*, 1924, i, 867.

[16] *Idem*, *ibid.*, 1925, **65**, 491; *A.*, 1926, 73.

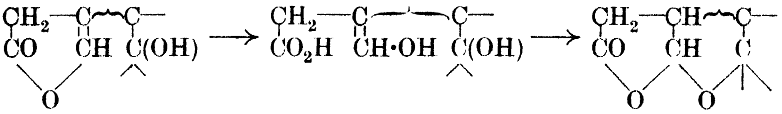
[17] W. A. Jacobs and E. L. Gustus, *ibid.*, 1927, **74**, 805; *A.*, 1927, 1194.

[18] W. A. Jacobs, A. Hoffmann, and E. L. Gustus, *ibid.*, 1926, **70**, 1; *A.*, 1926, 1250.

[19] W. A. Jacobs and A. Hoffmann, *ibid.*, 1927, **74**, 787; *A.*, 1927, 1194; compare M. Cloetta, *Arch. Exp. Path. Pharmakol.*, 1926, **112**, 324; *A.*, 1926, 755; A. Windaus, A. Bohne, and A. Schwieger, *Ber.*, 1924, **57**, 1388; *A.*, 1924, i, 1215. The difference is particularly marked in the glucosides themselves.

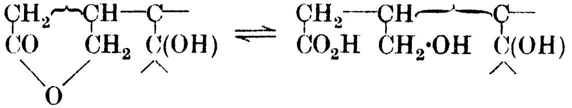
[20] *J. Biol. Chem.*, 1930, **87**, 601; *A.*, 1930, 1162.

[21] *Ibid.*, 1931, **93**, 139; *A.*, 1931, 1270.

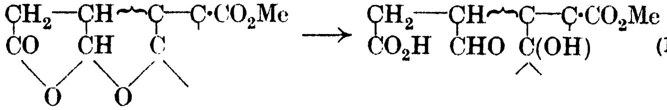


(I.) (II.) (III.)

The original compound is thus the lactone of a γ- or a δ-aldehydo-acid (II), here shown in its enolic modification, which undergoes a ring-chain tautomeric change of the type common in the sugars, with the formation of an oxide ring; the hydroxy-ring compound is then lactonised to the *iso*aglucone (III). This change is no longer observed with the dihydro-derivative, which is an inner anhydride of a saturated hydroxy-acid :



The formation of an aldehyde group on opening of the lactone ring has been shown as follows :[23] strophanthidinic ester gives an *iso*-compound on treatment with alkali. When the lactone ring of this substance is opened, *iso*strophanthidindiacid monomethyl ester (III*a*) is formed, the neutral ester of which readily forms a semicarbazone :



(III*a*.)

The aldehyde group formed by opening of the lactone ring of the *iso*-ester can also be oxidised to carboxyl by means of hypobromite, which is without action on the *iso*-ester itself. In all these compounds the original aldehyde group of strophanthidin is replaced by carbomethoxyl and complications are thus avoided.

There is evidence to show that there is an equilibrium between the aldehyde (open-chain) and the oxide form in derivatives of the

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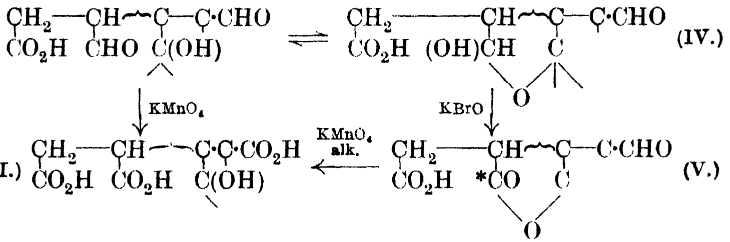
[22] W. A. Jacobs and A. M. Collins, *J. Biol. Chem.*, 1924, **61,** 387; *A.*, 1924, i, 1331.

[23] W. A. Jacobs and E. L. Gustus, *ibid.*, 1927, **74,** 805; *A.*, 1927, 1194.

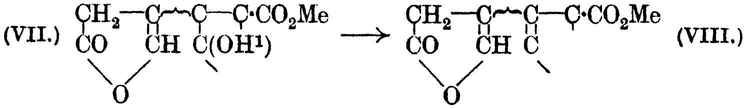
iso-compounds: when the lactone ring of *iso*strophanthidin is opened, the product, α-*iso*strophanthidinic acid (IV), reacts as an aldehyde with permanganate and gives α-*iso*strophanthic acid, (VI), both aldehyde groups being oxidised to carboxyls. Hypobromite, on the other hand, acts specifically on the oxidic form, giving the lactone, α-*iso*strophanthidic acid (V);[24] chromic acid acts in the same way, but oxidises the secondary hydroxyl group also.



The identity of the carboxyl group* taking part in lactone formation has been established with certainty.[23]

Both *iso*strophanthidin and *iso*strophanthidic acid exist in stereoisomeric α- and β-modifications, which are partly interconvertible in alkali, whereas the α- and β-*iso*strophanthic acids are no longer interconvertible. The *iso*strophanthic acids are further isomerised to γ- and δ-acids respectively; they differ in ease of lactonisation (on the secondary hydroxyl), only the δ-acid forming a lactone.[25]

Hydroxyl groups. To enable the strophanthidin–*iso*strophanthidin change to take place, it is necessary for one hydroxyl group (designated as OH^1) to be in the γ- or δ-position with respect to the aldehyde group concerned in the formation of the lactone ring, or in the α- or β-position to the carbon atom carrying the lactone side chain. This hydroxyl is also the one most easily removed; under the influence of alcoholic hydrogen chloride, strophanthidinic ester (VII) forms an anhydro-ester (VIII), which, unlike the parent ester, can no longer pass into an *iso*-compound:[26]



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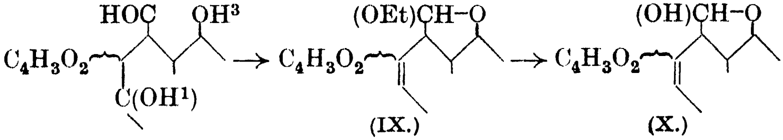
[24] W. A. Jacobs and A. M. Collins, *J. Biol. Chem.*, 1925, **65**, 491; *A.*, 1926, 73.

[25] W. A. Jacobs and E. L. Gustus, *ibid.*, 1927, **74**, 829; *A.*, 1927, 1194.

[26] *Idem, ibid.*, p. 795.

Strophanthidin itself undergoes a similar change, but a complication arises here due to the free aldehyde group; this reacts with a conveniently placed hydroxyl, forming a half-acetal (IX) : [27]

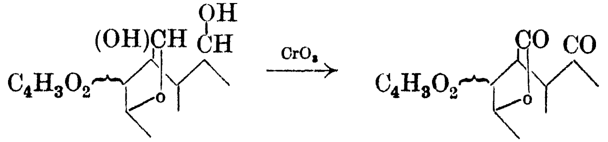


(IX.) (X.)

It is easy to show that the hydroxyl involved in acetal formation is the secondary one (OH^3) : the acetal can no longer be acylated, but this property is regained on hydrolysis to the free anhydrostrophanthidin (X), which also once more displays the properties of an aldehyde. It can therefore be concluded that the aldehyde group and OH^3 are in the γ- or δ-position to each other.

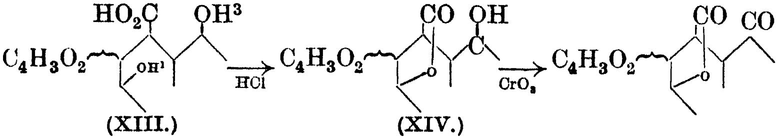
It has, however, been shown that another hydroxyl, namely OH^1, occupies a similar position with respect to the aldehyde group : strophanthidin undergoes cyclisation on treatment with concentrated hydrochloric acid to pseudostrophanthidin (XI),[28] which still retains OH^3 intact (oxidation to a ketone) [24] but is no longer capable of passing into an *iso*-compound on treatment with alkali. Moreover, pseudostrophanthidin is oxidised by chromic acid to a keto-dilactone [29] (XII), and the same substance is also obtained by

(XI.)



(XII.)

the oxidation with chromic acid of the dilactone (XIV) formed from strophanthidinic acid (XIII) with hydrochloric acid :



(XIII.) (XIV.)

The stability of this lactone ring may be noted in passing.

The relationships of the third hydroxyl group (OH^2) may now be examined. It is less easily removed than OH^1 : anhydrostrophanthidin requires fairly concentrated alcoholic hydrogen chloride for further dehydration, dianhydrostrophanthidin being then produced; this is again isolated in the form of an inner glucoside, formed, as

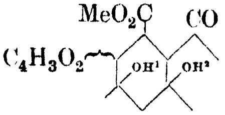
[27] W. A. Jacobs and A. M. Collins, *J. Biol. Chem.*, 1924, **59**, 713; *A.*, 1924, i, 867.

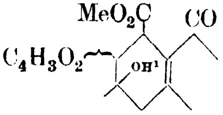
[28] *Idem, ibid.*, 1925, **63**, 123; *A.*, 1925, i, 566.

[29] W. A. Jacobs and E. L. Gustus, *ibid.*, 1927, **74**, 795; *A.*, 1927, 1194.

before, at the expense of OH^3.[27] If, however, the latter hydroxyl is previously oxidised, the ketonic compound so formed loses water with great ease. For example, the methyl ester of strophanthidinic acid on oxidation forms methyl strophanthidonate (XV), which readily gives the anhydro-compound (XVI):

(XV.)

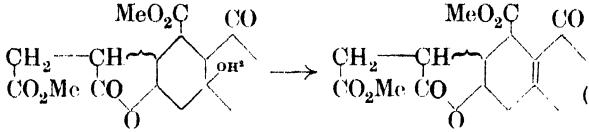




(XVI.)

Strophanthidinic ester gives an anhydro-compound by the loss of OH^1; this anhydro-compound can be oxidised to the ketonic ester, and this now loses water with great ease by the elimination of OH^2. Exactly similar reactions have also been observed in compounds of the *iso*-series, in which OH^1 is, of course, part of an oxide ring; thus, methyl *iso*strophanthonate (XVII) readily loses water:

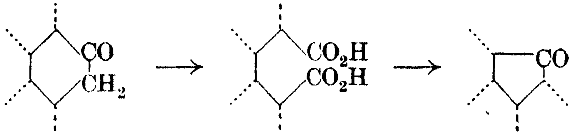
(XVII.)



(XVIII.)

It is therefore clear that OH^2 and OH^3 must be in the β-position to each other.[30]

Skeleton of strophanthidin. Of the four rings present in strophanthidin, that carrying the secondary hydroxyl group must be six-membered. A ketone obtained by the oxidation of a derivative of gitoxigenin* can be oxidised with the opening of this ring to a dibasic acid, which undergoes ring closure on heating and must therefore be an adipic or pimelic acid, and the original ring consequently six- or seven-membered:[31]



The latter possibility is disproved by W. A. Jacobs and E. L. Gustus,[32] who have shown that this ring † must be five- or six-membered, as follows: methyl *iso*strophanthonate gives, by the loss of OH^2, an anhydro-compound as already stated (p. 224). When this is oxidised with permanganate, the ring containing the keto-group is opened, with the production of carboxyl and a new keto-group. The process is formulated in the following rather unusual manner and is further discussed on p. 228:

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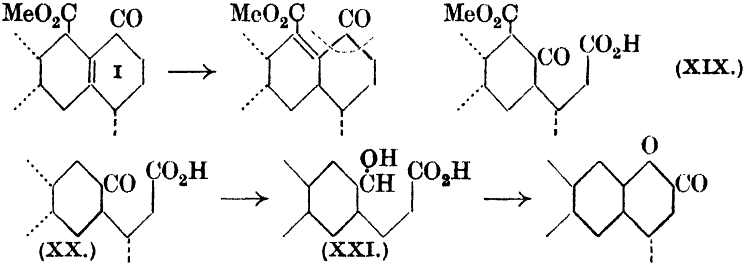
[30] W. A. Jacobs and E. L. Gustus, *J. Biol. Chem.*, 1927, **74**, 713; *A.*, 1927, 1194.

[31] A. Windaus, K. Westphal, and G. Stein, *Ber.*, 1928, **61**, 1847; *A.*, 1928, 1251.

[32] *J. Biol. Chem.*, 1928, **79**, 539; *A.*, 1928, 1376.

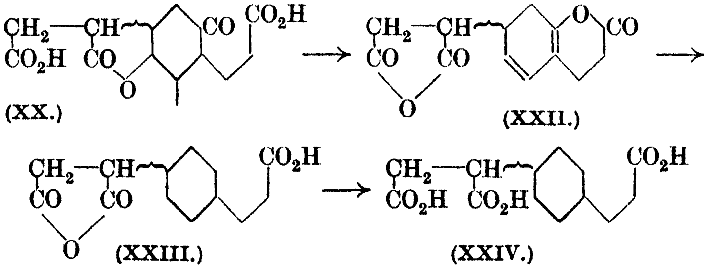
* The proof that the skeleton of gitoxigenin is identical with that of strophanthidin is given on p. 235.

† This ring is described as ring II in the original papers; it is here called ring I to avoid possible confusion.



The acid ester of undephanthontriacid (XIX) undergoes ketonic fission with the formation of the dimethyl ester of duodephanthondiacid (XX). This acid on reduction gives a hydroxy-acid (XXI), which is readily lactonised; the ring opened must therefore have been not more than six-membered.

The further degradation of duodephanthondiacid supplies additional information with regard to the ring which has been opened. The acid has been converted into the oxygen-free tribasic acid,[33] dephanthanic acid (XXIV), as follows: by the action of acetyl chloride and acetic anhydride the acid suffered a change characteristic of the *iso*-series,[34] the oxide ring being opened with the formation of an anhydride, and the hydroxyl OH^1 being removed; at the same time the unsaturated lactone (XXII) was formed.[35] The lactone ring opened on hydrogenation to the acid (XXIII) and finally the anhydride was hydrolysed:



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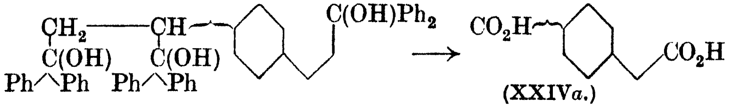
[33] W. A. Jacobs and R. C. Elderfield, *J. Biol. Chem.*, 1933, **102**, 237; *A.*, 1933, 1165.

[34] Compare W. A. Jacobs and E. L. Gustus, *ibid.*, 1929, **84**, 183; *A.*, 1929, 1456.

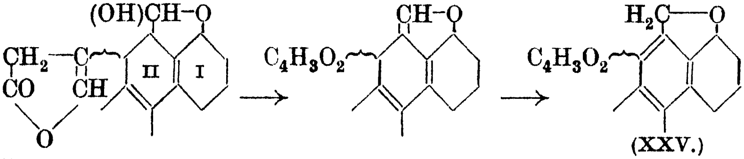
[35] *Idem*, *ibid.*, 1931, **92**, 323; *A.*, 1931, 1297.

When dephanthanic ester was subjected to the Wieland degradation with phenylmagnesium bromide,[36] four carbon atoms were lost in the production of dephanthic acid (XXIV*a*). This indicates that the lactone side chain had been completely removed and replaced by a carboxyl group; in addition, the side chain representing ring I had been shortened and, as a carboxyl group is formed here also, the carbon atom oxidised must have belonged to a CH_2 group, and no other ring could have been attached to ring I at that point. In other words, the six-membered ring opened in the oxidation of anhydro*iso*strophanthonic ester must occupy a terminal position.



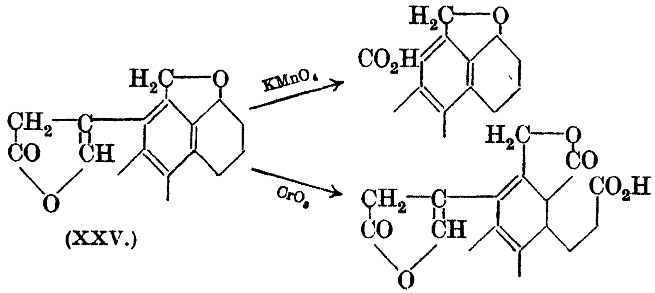
(XXIV*a*.)

The adjoining ring is also six-membered. This had originally been inferred from the formation of trianhydrostrophanthidin by the dehydration of the dianhydro-compound, which was represented as follows: [28]



(XXV.)

The aromatic character of one of the rings in this compound explains its resistance to reducing agents and has been confirmed by the nature of its absorption spectrum,[37] which is very similar to that of neoergosterol. Now on oxidation with permanganate the lactone side chain is completely removed and replaced by a carboxyl group;[38] this result was interpreted by assuming that the lactone side chain is attached directly to the ring which had become benzenoid, the action of chromic acid being similarly explained:



(XXV.)

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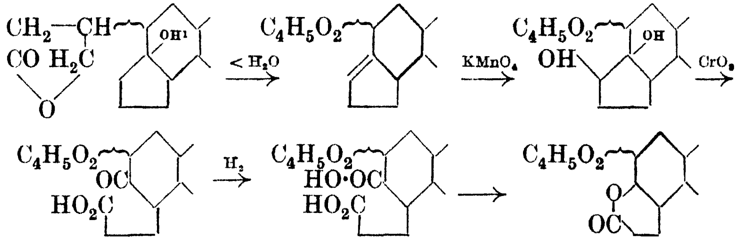
[36] H. Wieland, O. Schlichting, and R. Jacobi, *Z. physiol. Chem.*, 1926, **161**, 80; *A.*, 1927, 247.

[37] R. C. Elderfield and A. Rothen, *J. Biol. Chem.*, 1934, **106**, 71; *A.*, 1093.

[38] W. A. Jacobs and E. L. Gustus, *ibid.*, 1927, **74**, 805; *A.*, 1927, 1194.

The spectrum of the trianhydro-compound [37] shows no indication of the conjugation of a double bond with those of the benzene nucleus, such as would be expected if formula (XXV) were correct; and it has since become apparent that the formation of the compound probably involves a change in the skeleton, and its behaviour on oxidation also requires a different interpretation. The aromatic character of ring II has nevertheless been established by later work (see p. 230).

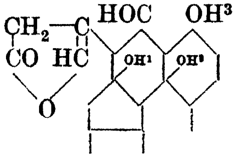
It has been ascertained that a CH_2 group must be adjacent to the tertiary carbon atom carrying OH^1 because, when this hydroxyl is eliminated from dihydrostrophanthidin and the resulting anhydro-compound is oxidised with permanganate, the glycol formed contains a secondary and a tertiary hydroxyl group; [39] the CHO group is oxidised to CO_2H at the same time. Further oxidation of the corresponding ester with chromic acid leads to the rupture of a ring, giving the keto-acid (XXVI):



(XXVI.)

Now the product of reduction of this keto-acid lactonises with great readiness, evidently to a γ- or δ-lactone; the two lactone rings in the latter compound (of which one is that originally present) readily open with alkali and close again on acidification. From this it follows that the ring which had been opened was five-membered at most. The identity of the hydroxyl group involved in these changes was established by showing that OH^2 and OH^3 were still intact and displayed the characteristic relationship described above, the former being eliminated with ease after oxidation of OH^3, but not before.

The facts already discussed were embodied in a partial formula (XXVII) for strophanthidin: [40]



(XXVII.)

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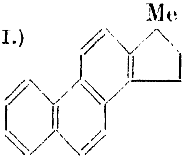
[39] W. A. Jacobs and R. C. Elderfield. *J. Biol. Chem.*, 1932, **97**, 727; *A.*, **1932**, **1138**.

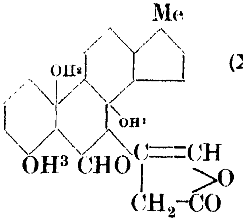
[40] *Idem, ibid.*, 1933, **102**, 237; *A.*, 1933, 1165.

New facts, however, soon necessitated its modification. In the first place, the dehydrogenation of strophanthidin with selenium[41] leads to Diels's hydrocarbon $C_{18}H_{16}$, which has recently been shown to have the structure (XXVIII)[42] and obtained from the sterols and also from uzarigenin.[43]

This suggests that the carbon skeleton of strophanthidin is closely related to that of the sterols; it is incompatible with the formula (XXVII), and is not satisfactorily explained by the adaptation of the latter such as (XXIX):[37]

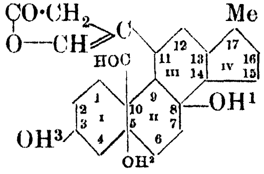
(XXVIII.)



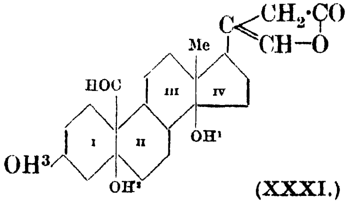


(XXIX.)

A further difficulty is presented by the oxidation of anhydro-*iso*strophanthonic ester; the mechanism put forward below is far from being convincing, as it presupposes a wandering of the double bond first formed, and there is no reason whatever for the loss of a carbon atom in the next stage, which might be expected to lead to the opening of ring II rather than I. To overcome these difficulties, a new formulation has been suggested,[44] in which the groups attached to ring I are arranged as in (XXX) and (XXXI):



(XXX.)



(XXXI.)

The oxidation of anhydro*iso*strophanthonic ester at once receives a satisfactory interpretation; it is analogous to that of cholestenone[45] and no longer necessitates the wandering of the double bond:

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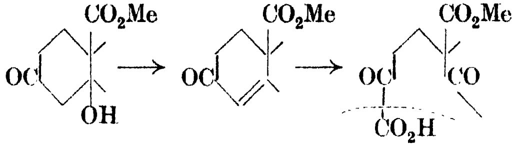
[41] W. A. Jacobs and R. C. Elderfield, *Science*, 1934, **79**, 279; *J. Biol. Chem.*, 1934, **107**, 143; *A.*, 657, 1359; compare W. A. Jacobs and E. E. Fleck, *Science*, 1931, **73**, 133; *A.*, 1931, 606; *J. Biol. Chem.*, 1932, **97**, 57; *A.*, 1932, 948.

[42] S. H. Harper, G. A. R. Kon, and F. C. J. Ruzicka, *J.*, 1934, 124; *A.*, 288; compare *Ann. Reports*, 1933, **30**, 213; H. Hillemann, *Ber.*, 1935, **68**, [*B*], 102.

[43] R. Tschesche and H. Knick, *Z. physiol. Chem.*, 1933, **222**, 58; *A.*, 193.

[44] G. A. R. Kon, *Chem. and Ind.*, 1934, **53**, 593; *A.*, 1007.

[45] *Ann. Reports*, 1933, **30**, 201.



The hydroxyl group OH^3, which is characteristic of all the aglucones, occupies the same position as it does in the sterols, and the aldehyde group is placed on the quaternary carbon atom which carries a methyl group in the latter compounds. The reason for this is that the hydrocarbon (XXVIII) is formed from both strophanthidin and uzarigenin; in the latter a methyl group takes the place of the aldehyde group (see p. 231). It is highly improbable that the same hydrocarbon would be obtained from both these compounds on dehydrogenation, unless the methyl or aldehyde group is attached to a quaternary carbon atom, in which case it would be eliminated altogether.

The only difference between the formulæ (XXX) and (XXXI) is the position of the lactone side chain and of OH^1, which must be in close proximity to it. The choice between these two arrangements is made possible by the determination of the crystal structure by the *X*-ray method, which has been carried out on several compounds of this group;[46] it shows that the lactone group cannot be attached to either of the middle rings, but must be accommodated on one of the terminal ones. This at once disposes of Kon's first formula (XXX) and also of (XXIX); strictly speaking, the evidence does not allow us to go further than that and several variants of formula (XXXI) apply equally well, although (XXXI) is particularly attractive from the biogenetic point of view.[47] The attachment of the lactone side chain to C_{17} has, however, been recently proved by R. Tschesche (p. 231) and by W. A. Jacobs and R. C. Elderfield (p. 233), and the correctness of the formula (XXXI) largely established; this has now been adopted by both the German and the American school.

Difficulties are encountered in endeavouring to explain the reactions of strophanthidin in the light of the new formulation; these arise mainly out of the distance separating OH^1 from the other hydroxyl groups, so that the dehydration of the aglucone becomes hard to interpret. The principal difficulty is the formation of trianhydrostrophanthidin, which cannot take place by the process described on p. 226. It is ring II which becomes benzenoid,[48] because on oxidation with nitric acid mellophanic acid is formed; the aldehyde group must wander from C_{10} to another position before the ring can become aromatic and the formula (XXXII) is proposed:

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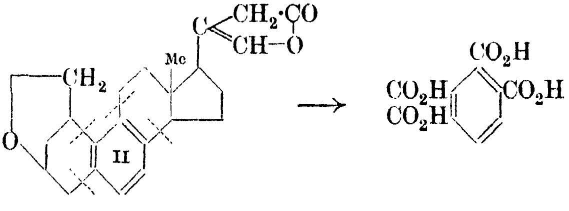
[46] J. D. Bernal and (Miss) D. Crowfoot, *Chem. and Ind.*, 1934, **53**, 593; *A.*, 1354.

[47] G. A. R. Kon, *ibid.*, p. 956; *A.*, 1355.

[48] R. Tschesche and H. Knick, *Z. physiol. Chem.*, 1934, **229**, 233.

(XXXII.)

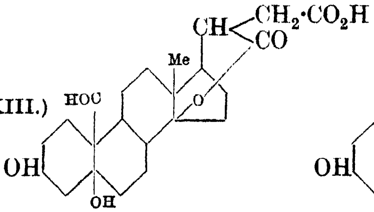


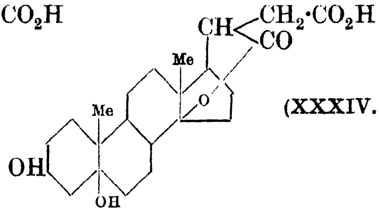
The interaction of the aldehyde group with OH^1 in the production of pseudostrophanthidin appears to involve some strain unless rings II and III are joined in the *cis*-position;* this interaction is therefore probably accompanied by a stereochemical change.

Observations [48a] which have been interpreted by assuming an interaction of a carboxyl resulting from the oxidation of the aldehyde group on C_{10} with a carboxyl in the lactone side chain need not be discussed in detail at this stage, as they are probably explicable in some other way.

Periplogenin.—The chemistry of this compound is very similar to that of strophanthidin [49] and it has recently been shown that the position of the aldehyde group in the latter is occupied by a methyl group in periplogenin; [50] this was accomplished by reducing the semicarbazone of *iso*strophanthidic acid (XXXIII) by the Kijner–Wolff method, *iso*periplogenic acid (XXXIV) being formed:

(XXXIII.)





(XXXIV.)

Uzarigenin.—This "genin" has not yet been obtained as such, but only in the form of the dianhydro-compound, $C_{23}H_{30}O_3$. The acetate of the latter can be hydrogenated to a mixture of stereoisomeric hexahydro-compounds. The last remaining hydroxyl group is secondary and can be oxidised with chromic acid; the ketonic compound so formed can be reduced by Clemmensen's method to two desoxo-compounds, one of which is identical with a compound derived from periplogenin.[51] These compounds therefore have the same skeleton. The secondary hydroxyl group of uzarigenin is situated in a terminal six-membered ring, because the hexahydro-compound mentioned above can be oxidised to a dibasic acid giving a ketone on pyrolysis.

[48a] W. A. Jacobs and R. C. Elderfield, *J. Biol. Chem.*, 1932, **96**, 357; *A.*, 1932, 748.

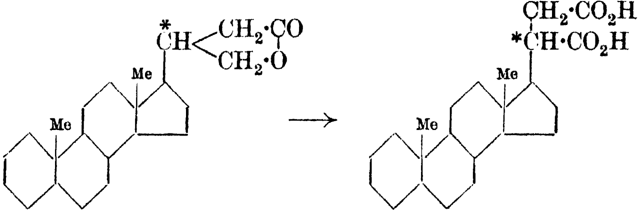
[49] W. A. Jacobs and A. Hoffmann, *ibid.*, 1928, **79**, 519; *A.*, 1928, 1359; W. A. Jacobs and R. C. Elderfield, *ibid.*, 1931, **91**, 625; *A.*, 1931, 827.

[50] W. A. Jacobs, R. C. Elderfield, T. B. Grave, and E. W. Wignall, *ibid.*, p. 617; *A.*, 1931, 826.

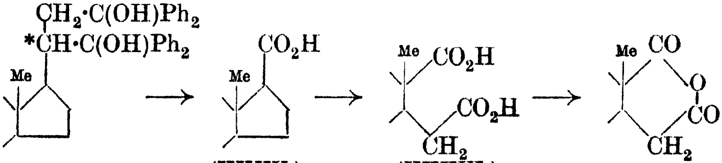
* Private communication from Prof. W. A. Jacobs.

Quite recently [52] Tschesche proved that the lactone group in these compounds, and therefore also in the other aglucones of the strophanthidin group, is attached to C_{17} and, moreover, that the remainder of their skeleton is identical with that of the sterols.

Starting with the two desoxo-lactones mentioned above, he obtained by vigorous oxidation with chromic acid two stereoisomeric dibasic acids, $C_{23}H_{36}O_4$, produced by the opening of the lactone ring:



When the esters of these two acids were degraded by Wieland's method, the same monobasic acid, $C_{20}H_{32}O_2$ (XXXV), analogous to dephanthanic acid (p. 225), was formed from both; this shows that the two lactones were stereoisomeric about the carbon atom *:



(XXXV.) (XXXVI.)

A repetition of the degradation process led to a dibasic acid (XXXVI), which gave an anhydride on pyrolysis; it can therefore be concluded (i) that the lactone side chain had been attached *directly* to a ring, (ii) that this ring was five-membered, since it is a terminal ring and Blanc's rule would therefore be expected to apply,[53] and (iii) that a CH_2 group must be adjacent to the point of attachment of the lactone ring.

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[51] R. Tschesche, *Z. physiol. Chem.*, 1933, **222**, 50; *A.*, 1934, 193.

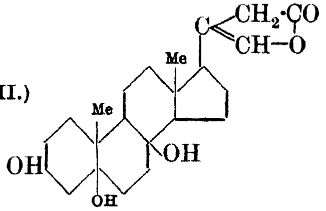
[52] *Ibid.*, 1934, **229**, 219; *Angew. Chem.*, 1934, **47**, 729; *A.*, 1354.

[53] Compare *Ann. Reports*, 1933, **30**, 200.

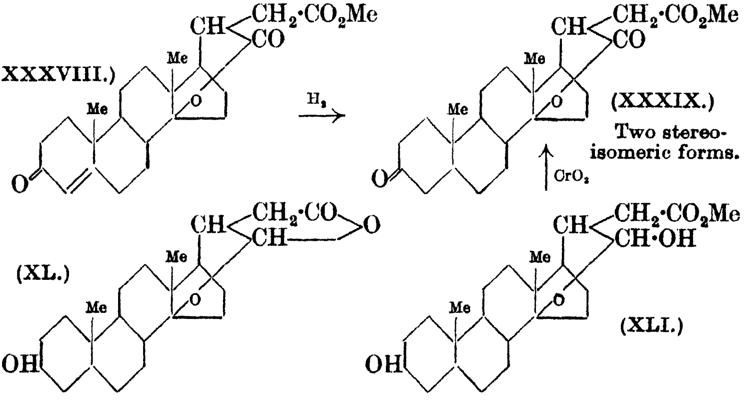
The C_{20} acid is not identical with ætiocholanic acid and is termed *allo*ætiocholanic acid; it should therefore result from the degradation of *allo*cholanic acid. Two steps in this degradation have already been carried out;[54] the third proved troublesome, but a small amount of an acid with the properties of the C_{20} acid was isolated.[52] Their identity having been established,[52a] the important conclusion can be drawn that the carbon skeleton of uzarigenin is identical with that of the sterols, the lactone ring taking the place of the side chain attached to C_{17}. This is further supported by the work described on p. 233.

Uzarigenin is incapable of passing into an *iso*aglucone and therefore probably lacks the necessary hydroxyl, OH^1, attached to C_{14}; the following formula is considered by Tschesche to be the most probable:

(XXXVII.)



Digitoxigenin.—This aglucone also is very similar to strophanthidin;[55] it differs from periplogenin in not having the tertiary



(XXXVIII.) (XXXIX.) Two stereoisomeric forms. (XL.) (XLI.)

[52a] R. Tschesche, *Ber.*, 1935, **68**, [*B*], 7.

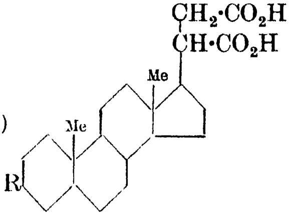
[54] C. K. Chuang, *Annalen*, 1933, **500**, 270; E. Fernholz, *ibid.*, 1933, **507**, 128; *A.*, 1933, 391, 1290.

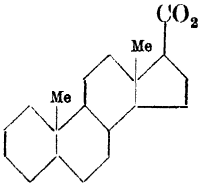
[55] W. A. Jacobs and E. L. Gustus, *ibid.*, 1928, **78**, 573; *A.*, 1928, 1120; M. Cloetta, *Arch. Exp. Path. Pharmakol.*, 1920, **88**, 138; *A.*, 1921, i, 39; A. Windaus and G. Bandte, *Ber.*, 1923, **56**, 2001; *A.*, 1923, i, 1107; A. Windaus and G. Stein, *ibid.*, 1928, **61**, 2436; *A.*, 1929, 71.

hydroxyl OH^2. This was proved [56] by oxidising the methyl ester of *iso*periplogenic acid (XXXIV) with chromic acid to the ketonic ester, which now readily lost water with the elimination of OH^2 as usual; the anhydro-compound (XXXVIII) was hydrogenated to a mixture of two stereoisomeric dihydro-compounds (XXXIX), m. p. 251° and 192—193·5°, the second of which was identical with an ester prepared from digitoxigenin. The latter [57] forms an *iso*aglucone (XL) under the influence of alkali, and this, on opening of the lactone ring, gives *iso*digitoxigeninic acid, the methyl ester of which (XLI) is oxidised by chromic acid to *iso*digitoxigonic ester, m. p. 192—193·5°.

W. A. Jacobs and R. C. Elderfield [58] have carried out a series of degradations essentially similar to those of Tschesche (p. 231): γ-digitoxanoldiacid (XLII, R = OH) was converted, through the ketonic acid, into the digitoxandiacid (XLII, R = H). The ester of this was subjected to degradation by Wieland's method, ætiocholanic acid (XLIII) being obtained:

(XLII.)





(XLIII.)

These results constitute an independent proof of the identity of the skeleton of the cardiac aglucones and the bile acids. It might also be concluded from this that the cardiac aglucones belong stereochemically to the bile acid, not the sterol, series; but in the conversion of digitoxigenin into an acid of the γ-series a change of configuration is not excluded. On the other hand, Tschesche rightly points out [52a] that the conversion of uzarigenin into *allo*-cholanic acid does not prove that this aglucone belongs to the sterol series, because the change probably involves the elimination of a hydroxyl attached to C_5 with the consequent possibility of steric inversion about this atom.

Gitoxigenin.—The chemistry of this aglucone is in some ways more complex than that of the others. A. Windaus and C. Freese [59] suspected that gitoxigenin is a hydroxydigitoxigenin, but were unable to prove it: gitoxigenin readily lost two molecules of water, forming the dianhydro-compound, identical with bigitaligenin;[60] a secondary hydroxyl group still remaining was situated in a ring of not less than six members (p. 224), and on hydrogenation the compound yielded a hexahydro-derivative isomeric with tetrahydroanhydrodigitoxigenin.

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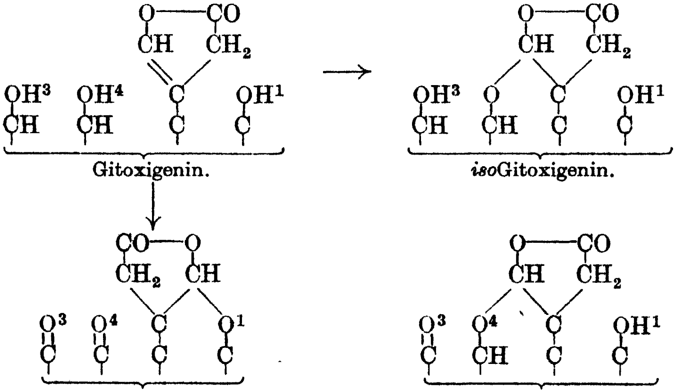
[56] W. A. Jacobs and R. C. Elderfield, *J. Biol. Chem.*, 1931, **92**, 313; *A.*, 1931, 1297.

[57] W. A. Jacobs and E. L. Gustus, *ibid.*, 1928, **78**, 573; *A.*, 1928, 1120.

[58] W. A. Jacobs and R. C. Elderfield, *Science*, 1934, **80**, 434; *A.*, 1935, 88; *J. Biol. Chem.*, in the press. The Reporter is indebted to Prof. W. A. Jacobs for a copy of his MS.

[59] *Ber.*, 1925, **58**, 2503; *A.*, 1926, 153.

Jacobs and his collaborators established the relationship between these two aglucones in the *iso*-series. Gitoxigenin, like other aglucones, forms an *iso*aglucone,[61] but this is more resistant to hydrolysis than other compounds of this class;[62] *iso*gitoxigeninic acid, produced on opening of the lactone ring, does not show the reactions of an aldehyde, as its ester does not react with ketonic reagents. The reason for this and other abnormal reactions of *iso*gitoxigenin is[63] that the hydroxyl involved in the formation of the *iso*-ring is a secondary one. Thus, although the original aglucone forms a dibenzoate, *iso*gitoxigenin forms a monobenzoate; similarly, the *iso*-compound is oxidised by chromic acid to a monoketone,[62] whereas the parent compound gives a diketone, gitoxigenone.[61] The latter compound, unlike the corresponding digitoxigenone, is saturated, owing to the fact that it is also an *iso*-compound and as such no longer forms an anhydro-derivative. In its formation the tertiary hydroxyl group OH^1 must be involved:[63]



Gitoxigenin. *iso*Gitoxigenin.

Gitoxigenone. *iso*Gitoxigenone.

It must therefore be concluded that in gitoxigenin *iso*aglucone formation is possible in two directions, one involving the secondary hydroxyl, and the other the tertiary one. Normally, the first process is favoured, but the second operates if the relevant CH·OH group is oxidised to CO.

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[60] M. Cloetta, *Arch. Exp. Path. Pharmakol.*, 1926, **112**, 260; *A.*, 1926, 755.

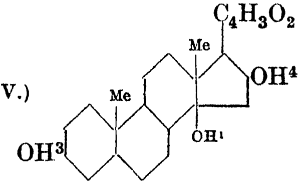
[61] W. A. Jacobs and E. L. Gustus, *J. Biol. Chem.*, 1928, **79**, 553; *A.*, 1928, 1376.

[62] *Idem*, *ibid.*, 1929, **82**, 403; *A.*, 1929, 798.

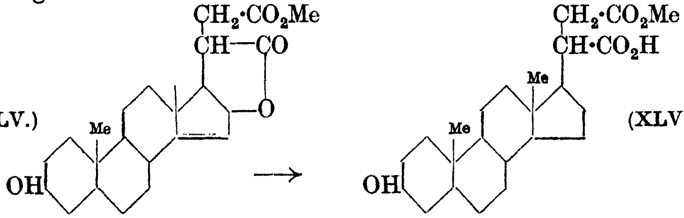
[63] *Idem*, *ibid.*, 1930, **88**, 519; *A.*, 1930, 1413.

Dihydrogitoxigenin also is oxidised to a diketone, in which the conversion into an *iso*-compound is of course impossible; it readily loses water (dihydroditoxigenone is stable under identical conditions) and it can be inferred that the removal of OH^1 is due to the influence of the carbonyl group characteristic of gitoxigenone. W. A. Jacobs and R. C. Elderfield [64] suggest that this is due to the tendency of the carbonyl group to enolise and assume that OH^1 and OH^4 are in the 1 : 4-position to each other. This finds a more ready expression in the formula (XLIV) for gitoxigenin,[65] the hydroxyls being relatively in the β-position.

(XLIV.)



The correlation of gitoxigenin with digitoxigenin was a matter of some difficulty, because the additional hydroxyl group of the former compound could not readily be replaced by hydrogen. Finally,[66] *iso*gitoxigenic acid, in which the extra hydroxyl is concerned in ring formation, was converted into the anhydro-compound by the removal of OH^1 (through the chloro-derivative and with the simultaneous stereoisomerisation to the γ-series); when the ester of the anhydro-compound (XLV) was hydrogenated, the lactone ring was opened and the hydroxyl liberated was replaced by hydrogen:


(XLV.) (XLVI.)

The same substance was also produced from *iso*digitoxigenic acid (XLVII) as follows: the acid, when heated with hydrochloric acid, was converted into the γ-stereoisomeride, which, on treatment with acetyl chloride and acetic anhydride lost water and underwent a change analogous to that described on p. 226. The secondary hydroxyl group was acetylated at the same time; the anhydride ring was opened with methyl-alcoholic hydrogen chloride, the product hydrogenated to the ester (XLVIII), and this hydrolysed to γ-digitoxanoldiacid (XLIX), identical with the product of hydrolysis of the acid ester (XLVI) from gitoxigenin.

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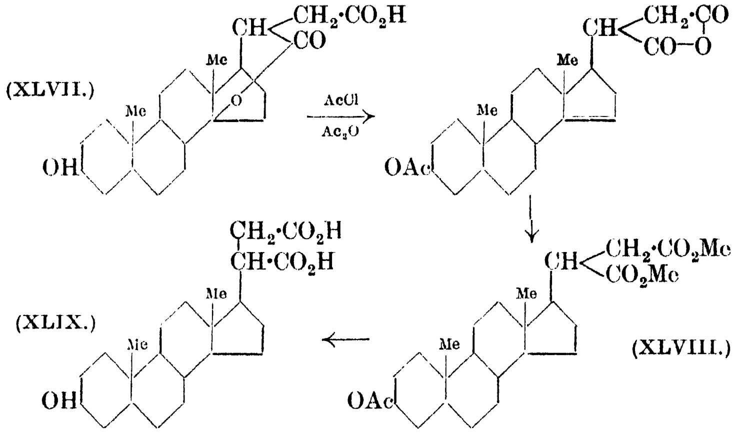
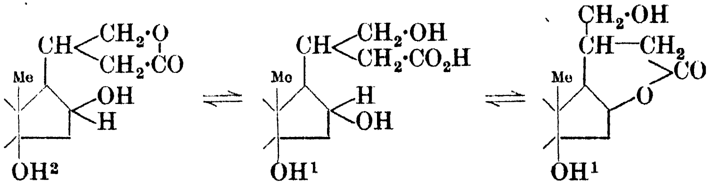
[64] *J. Biol. Chem.*, 1933, **100**, 671; *A.*, 1933, 700.

[65] R. Tschesche, *Z. physiol. Chem.*, 1934, **229**, 219; W. A. Jacobs and R. C. Elderfield, in the press.

[66] W. A. Jacobs and E. L. Gustus, *J. Biol. Chem.*, 1930, **86**, 199; *A.*, 1930, 749.


(XLVII.) (XLVIII.) (XLIX.)

Gitoxigenin is hydrogenated to two substances,[67] subsequently found to be isomeric dihydro-compounds,[68] the α- being dextro- and the β- lævo-rotatory. Their property of mutarotation [69] suggested that they differ owing to the lactone group being formed with two different hydroxyl groups, one of which (in the β-compound) must be the characteristic secondary hydroxyl group, OH^4, of gitoxigenin. In agreement with this, a mixture of diacetates is formed on acetylation; the β-compound forms a lævorotatory diacetate, and the dextrorotatory diacetate of the α-form is also produced by the direct hydrogenation of gitoxigenin diacetate:



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[67] M. Cloetta, *Arch. Exp. Path. Pharmakol.*, 1926, **112**, 285; *A.*, 1926, 755.

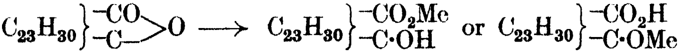
[68] A. Windaus, K. Westphal, and G. Stein, *Ber.*, 1928, **61**, 1847; *A.*, 1928, 1251.

[69] W. A. Jacobs and R. C. Elderfield, *J. Biol. Chem.*, 1933, **100**, 671; *A.*, 1933, 700.

Ouabagenin.—Little is known regarding this substance beyond the fact that it is an unsaturated lactone.[70] The "genin" is combined with rhamnose in ouabain and has not yet been isolated because the drastic treatment required to effect cleavage of the glucoside produces secondary changes. Anhydro-ouabain hepta-acetate,[71] produced by the acetylation of ouabain in the presence of zinc chloride, can, however, be hydrolysed, after previous hydrogenation, to a crystalline acetate, $C_{24}H_{30}O_4$, from which the free hydroxy-lactone, $C_{22}H_{28}O_3$, can be obtained; one carbon atom of the original aglucone has therefore been lost (as formaldehyde), also four presumably tertiary hydroxyl groups.[72] It is suggested that the tetra-anhydro-ouabain intermediately produced contains the group $\begin{matrix}C\\C\end{matrix}\!\!>C{:}CH_2$, which then gives rise to formaldehyde, but it is difficult to see how such an arrangement could be formed on the basis of the skeleton common to the cardiac aglucones, unless it is the result of a pinacolic change.

Acetolysis of *iso*ouabain similarly leads to the acetate of a tri-anhydro*iso*aglucone; the free compound is also a C_{22} derivative and extremely resistant to hydrogenation, thus resembling trianhydrostrophanthidin. The remaining hydroxyl group is secondary and can be oxidised to a keto-group; it is presumably identical with OH^3 of the other "genins." Similarly, OH^1 probably takes part in the formation of the *iso*aglucone oxide ring, but is lost in the formation of the tetra-anhydro-compound, $C_{22}H_{28}O_3$, obtained from ouabain itself.[73]

Scillaridin A.—This aglucone differs somewhat from those previously described; it contains two more carbon atoms and, although it is an unsaturated lactone, does not give the Legal nitroprusside reaction (compare p. 220). Under the influence of alcoholic alkali, it forms an *iso*aglucone containing methoxyl or ethoxyl according to the alcohol employed; [74] the anhydro-compound behaves in the same way:



$$C_{23}H_{30}\left\}\begin{matrix}-CO\\-C\end{matrix}\right.\!\!>O \longrightarrow C_{23}H_{30}\left\}\begin{matrix}-CO_2Me\\-C{\cdot}OH\end{matrix}\right. \text{ or } C_{23}H_{30}\left\}\begin{matrix}-CO_2H\\-C{\cdot}OMe\end{matrix}\right.$$

(L.) (LI.)

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[70] W. A. Jacobs and A. Hoffmann, *J. Biol. Chem.*, 1926, **67**, 333; 1927, **74**, 787; *A.*, 1926, 430; 1927, 1109.

[71] A. Arnaud, *Compt. rend.*, 1898, **126**, 1654; *A.*, 1898, i, 677.

[72] W. A. Jacobs and N. M. Bigelow, *J. Biol. Chem.*, 1932, **96**, 647; *A.*, 1932, 856.

[73] *Idem, ibid.*, 1933, **101**, 15; *A.*, 1933, 829.

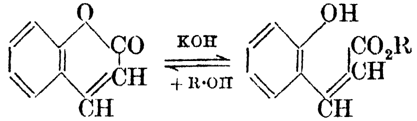
[74] A. Stoll, A. Hofmann, and A. Helfenstein, *Helv. Chim. Acta*, 1934, **17**, 641; *A.*, 636.

The entering alkyl group causes esterification, for the product (L) is still acidic, as it retains a phenolic hydroxyl group; it becomes neutral on hydrogenation: the alternative formula (LI) would lead to a carboxylic acid. The compound (L), anhydroscillaridinic ester, is easily hydrolysed, giving anhydroscillaridin when the solution is acidified.

The free hydroxyl of scillaridin is evidently tertiary and capable of interacting with the carboxyl of the lactone ring, as already stated, but this change does not cause the disappearance of a double bond; also, the lactone ring can be opened to give scillaridinic ester without isomerisation to the *iso*-series; this can be prevented altogether by the etherification of the phenolic hydroxyl liberated by the opening of the lactone ring. This behaviour constitutes a characteristic of scillaridin A as compared with the other aglucones. Also, once the formation of the oxide bridge (*iso*aglucone formation) has taken place, the carboxyl no longer forms a lactone ring.

These compounds therefore exhibit a behaviour similar to that of the coumarins and it must be inferred that they contain the characteristic group (LII):

(LII.)



In agreement with this, scillaridin A contains four double bonds, and the anhydro-compound five,[75] yielding octa- and deca-hydro-compounds respectively on hydrogenation; the lactone group also undergoes fission to some extent, a saturated acid being formed as a by-product. This behaviour suggests an unsaturated lactone *without* a substituent attached to the β-carbon atom [20, 21]; in this respect, therefore, scillaridin A differs from the aglucones of the strophanthidin group.

Toad Poisons.

This group of substances, though of animal origin, appears to be closely related to the cardiac aglucones. They are present in the secretion of certain glands of toads, one such secretion constituting the Chinese drug Ch'an Su; they have a characteristic action on the heart, similar to that of digitalis. The first of them, bufagin, was discovered by J. J. Abel and D. I. Macht.[76]

Later work tends to show that these compounds are mostly present, not as such, but in combination. The secretion of the European toad, from which bufotalin was originally obtained,[77] contains bufotoxin, $C_{40}H_{62}O_{11}N_4$,[78] which is hydrolysed to arginine, suberic acid, and the non-nitrogenous "genin," bufotalin, $C_{26}H_{36}O_6$. The last is esterified with suberylarginine, somewhat in the same way as the aglucones of plant origin are united to sugars. Gamabufotoxin,[79] obtained from the secretion of the Japanese toad, is also a suberylarginine derivative, but is derived from a different "genin," gamabufogenin, $C_{24}H_{34}O_5$. Both these toxins are hydrolysed by acids with the loss of water, forming anhydro-compounds.

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[75] A. Stoll, A. Hofmann, and W. Kreis, *Helv. Chim. Acta*, 1934, **17**, 1334; *A.*, 1206.

[76] *J. Pharm. Exp. Ther.*, 1911, **3**, 319; *A.*, 1912, ii, 1193.

Ch'an Su contains cinobufotoxin,[80] the "genin" of which is cinobufagin, $C_{25}H_{32}O_6$. Bufagin from the tropical *Bufo Marinus* is $C_{24}H_{32}O_5$.[81]

Bufotalin is the acetate of a trihydroxy-lactone, $C_{24}H_{34}O_5$. One hydroxyl is secondary, oxidation with chromic acid producing the ketone bufotalone. Concentrated hydrochloric acid removes two other hydroxyls, which are presumably tertiary, forming the coloured bufotalien, $C_{24}H_{30}O_3$, containing four double bonds,[78] and this has been hydrogenated to the saturated alcohol, bufotalan, $C_{24}H_{38}O_3$. The same sequence of operations has been carried out with acetylbufotalien, leading to acetylbufotalan; a by-product is an acetoxycholanic acid, $C_{26}H_{42}O_4$, in which the lactone group has been opened and reduced to a saturated side chain.[82] The remaining secondary hydroxyl group was eliminated by removing the acetyl group and heating, the cholenic acid formed being then reduced to the saturated *iso*bufocholanic acid, $C_{24}H_{40}O_2$. This was done in the hope of correlating bufotalin with the bile acids, but the cholanic acid so formed was different from the isomerides already known, including one derived from the bile of toads; this may, of course, be due to stereoisomerism arising out of the formation of isomerides on hydrogenation; otherwise, it means that the carbon skeleton of bufotalin is not identical with that of the bile acids.

One of the double bonds of bufotalien must be in the lactone side chain, because only unsaturated lactones are known to undergo fission on hydrogenation; in agreement with this, the saturated bufotalan does not undergo this change. It is at present undecided whether the double bond is already present as such in the lactone ring, or is formed by the elimination of water from a hydroxylactone such as

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[77] H. Wieland and F. J. Weil, *Ber.*, 1913, **46**, 3315; *A.*, 1913, i, 1343.

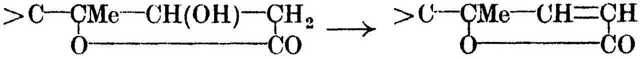
[78] H. Wieland and R. Alles, *ibid.*, 1922, **55**, 1789; *A.*, 1922, i, 784.

[79] H. Wieland and F. Vocke, *Annalen*, 1930, **481**, 215; *A.*, 1930, 1466.

[80] H. Jensen and K. K. Chen, *J. Biol. Chem.*, 1930, **87**, 741; *A.*, 1930, 1205.

[81] H. Jensen, *Science*, 1932, **75**, 53; *A.*, 1932, 397; see also K. K. and A. L. Chen, *J. Pharm. Exp. Ther.*, 1933, **49**, 503 *et seq.*; *A.*, 1934, 324.

[82] H. Wieland, G. Hesse, and H. Meyer, *Annalen*, 1932, **493**, 272; *A.*, 1932, 397.



$$\begin{array}{l}>\mathrm{C{-}CMe{-}CH(OH){-}CH_2}\\ \quad\mathrm{O}\text{————————}\mathrm{CO}\end{array}\longrightarrow\begin{array}{l}>\mathrm{C{-}CMe{-}CH{=}CH}\\ \quad\mathrm{O}\text{—————}\mathrm{CO}\end{array}$$

Like scillaridin A, bufagin does not give the Legal nitroprusside reaction and differs in this respect from the aglucones of the strophanthidin group.[83] Bufagin on hydrolysis gives formic acid,[81] and cinobufagin yields acetic acid; it could therefore be concluded that they are, respectively, the formyl and the acetyl derivative of a " genin " with 23 carbon atoms. The latest work of H. Jensen and E. A. Evans indicates, however,[84] that the formic acid obtained from bufagin on hydrolysis is in reality derived from formaldehyde, which is doubtless formed by the fission of a group $>\mathrm{C{:}CH_2}$, just as in the case of ouabain.[85] Apart from this, bufagin and cinobufagin have been shown to possess two double bonds by the formation of tetrahydro-derivatives, and a secondary hydroxyl group which can be acetylated and is oxidised by chromic acid with the production of a ketone. There are two apparently tertiary hydroxyls which are readily eliminated with the formation of dianhydro-compounds, $C_{24}H_{28}O_3$. These reactions are quoted to indicate the similarity in behaviour of the toad poison " genins " and the cardiac aglucones; their final correlation must await further experimental work, which is rendered extremely difficult by the scarcity of the starting material.

G. A. R. K.

Free Radicals.

Long Life.—In a previous Report [87] attention was drawn to a determination [86] of the heat of dissociation of the $\vdots\mathrm{C{-}C}\vdots$ bond in hexaphenylethane, which was found to be 11·5 kg.-cals. per mol. and practically independent of the solvent, compared with 71 kg.-cals. for the analogous bond in unsubstituted ethanes.[88] S. Goldschmidt and J. Bader [89] found the heat of dissociation of the $:\mathrm{N{-}N}:$ bond in dibenzoyltetraphenyltetrazan to vary from 5·2 kg.-cals. in chloroform to 10·5 kg.-cals. in toluene, and in spite of this considerable dependence on the solvent it may be concluded that the energy necessary for the fission of the $:\mathrm{N{-}N}:$ bond in a tetrazan is only about one-tenth of that necessary for the same purpose in an ordinary non-radical-forming nitrogen compound (90 kg.-cals.). Attempts were made to follow the velocity of dissociation of hexaphenylethane by the addition of a reagent susceptible to determination which reacted instantly with triphenylmethyl, but did not itself influence the dissociation of hexaphenylethane. Earlier experiments with oxygen [90, 91] were inconclusive owing to the formation of a labile, easily dissociated peroxide [92] which initiated chain reactions: [93]

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[83] K. K. Chen and A. L. Chen, *J. Pharm. Exp. Ther.*, 1933, **47**, 561; *A.*, 1933, 530.

[84] *J. Biol. Chem.*, 1934, **104**, 307; *A.*, 412.

[85] This Report, p. 237.

[86] K. Ziegler and L. Ewald, *Annalen*, 1929, **473**, 163; *A.*, 1929, 1010.

[87] *Ann. Reports*, 1930, **27**, 125.

[88] K. Fajans, *Ber.*, 1922, **55**, 2829; *A.*, 1922, ii, 818.

[89] *Annalen*, 1929, **473**, 137; *A.*, 1929, 1173.

$$R\cdot + O_2 = RO_2\cdot;\ RO_2\cdot + R{-}R = R{\cdot}RO_2 + R\cdot$$

Pyrogallol, however, inhibits their propagation, and in its presence exactly one molecule of oxygen is absorbed per molecule of triphenylmethyl, with the probable formation of triphenylmethyl hydroperoxide.[94] The anomalies apparent in the earlier experiments [90, 91] then disappear, and the reaction follows the strictly unimolecular course ascertained by the use of halogens [95] and nitric oxide.[96] The latter is the most suitable reagent for determining dissociation velocities of hexa-arylethanes, and with its aid the period of half-change of hexaphenylethane, 3·3 minutes, was found to be almost independent of the solvent in the sixteen cases investigated, and the activation energy was 19—20 kg.-cals. between − 20° and + 10°.

E. Hückel [97] has considered how the small energy of dissociation of the substituted ethanes can be explained in terms of their atomic and electronic configurations. The problem was solved by the Herzberg–Hund–Mulliken method and the results indicate, in agreement with experiment, that for the hexa-arylethanes the bond strain by resonance is greater, *i.e.*, the energy of dissociation is smaller, as the size of the substituent becomes greater, and that replacement of aromatic by aliphatic substituents diminishes the bond strain and therefore increases the energy of dissociation considerably, thus giving a mathematical significance to the experimental fact that a sufficient number of aromatic (or unsaturated) groups is a necessary condition for the existence of free aryl radicals.

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[90] K. Ziegler, L. Ewald, and P. Orth, *Annalen*, 1930, **479**, 277; *A.*, 1930, 711.

[91] R. C. Mithoff and G. E. K. Branch, *J. Amer. Chem. Soc.*, 1930, **52**, 255 *A.*, 1930, 301.

[92] K. Ziegler and P. Orth, *Ber.*, 1932, **65**, [*B*], 628; *A.*, 1932, 611.

[93] K. Ziegler and L. Ewald, *Annalen*, 1933, **504**, 162; *A.*, 1933, 943.

[94] H. Wieland and J. Maier, *Ber.*, 1931, **64**, 1207; *A.*, 1931, 839.

[95] K. Ziegler and P. Orth, *Annalen*, 1930, **479**, 292; *A.*, 1930, 711.

[96] K. Ziegler, P. Orth, and K. Weber, *ibid.*, 1933, **504**, 131; *A.*, 1933, 943.

[97] *Z. Physik*, 1933, **83**, 632; *Trans. Faraday Soc.*, 1934, **30**, 40; *A.*, 1933, 890, 1138; *Ann. Reports*, 1933, **30**, 46.

Hückel correctly places Conant's monoaliphatic diarylmethyls [98, 99] as free radicals.

L. Pauling and H. Wheland [1] regard dissociation as being due not so much to a weak ⁝C–C⁝ bond as to resonance among structures in which the unpaired electron is on the methyl carbon atom and those where it is on another atom. This treatment is similar to that of C. K. Ingold and H. Burton,[2] in which radical stability is ascribed to the "degeneracy" of a large number of tautomeric forms, and although Ingold's theory is essentially descriptive and qualitative, its wide purview makes it valuable from the purely chemical standpoint.[3]

One of the fundamental premises of Hückel's theory [97] is the existence of a plane triphenylmethyl radical. Earlier attempts to establish the spatial configuration of the molecule [4, 5] were inconclusive, but more recently, E. S. Wallis and F. H. Adam [6] have concluded that, whereas CAr_3^- and CAr_3^+ can exist in an optically active state, the free radicals, whether they be of the classical triphenylmethyl type, or of the mixed aliphatic-aromatic type, cannot maintain the asymmetric configuration of the corresponding quadricovalent compounds from which they are derived. It must be concluded, therefore, that either the three substituents and the central carbon atom become coplanar, or if a non-planar arrangement is maintained, an oscillation of the groups around the central carbon atom occurs. On the other hand,[7] on irradiation of phenyl-*p*-tolyl-*p*-ethylphenylmethyl with circularly polarised light (4300 Å.) in the presence of chlorine at 0°, addition occurred, whereby an optical activity of 0·1° was obtained, and with phenyldiphenylyl-α-naphthylmethyl 0·2° was measured, which was reversed by irradiation with circularly polarised light of wave-length 5890 Å. The triarylmethyls are therefore mixtures of two optical antipodes, and the three carbon valencies cannot lie in one plane. The publication of the full experimental details of this total asymmetric synthesis with its important implications is awaited with interest.

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[98] J. B. Conant and N. M. Bigelow, *J. Amer. Chem. Soc.*, 1928, **50**, 2641; *A.*, 1928, 994.

[99] J. B. Conant and R. F. Schultz, *ibid.*, 1933, **55**, 2098; *A.*, 1933, 703.

[1] *J. Chem. Physics*, 1933, **1**, 362; *C.A.*, 1933, **27**, 3877.

[2] *Proc. Leeds Phil. Soc.*, 1929, **1**, 421; *J.*, 1933, 1120; *A.*, 1929, 1052; 1933, 1151.

[3] C. K. Ingold, *Trans. Faraday Soc.*, 1934, **30**, 52; *A.*, 242.

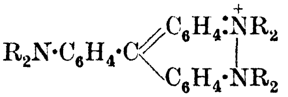
[4] J. Schmidlin and R. V. Escher, *Ber.*, 1912, **45**, 889; *A.*, 1912, i, 437.

[5] E. S. Wallis, *Proc. Nat. Acad. Sci.*, 1930, **16**, 215; *J. Amer. Chem. Soc.*, 1931, **53**, 812, 2253; *A.*, 1930, 773; 1931, 480, 1050.

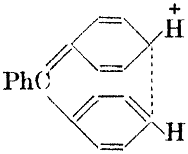
[6] *J. Amer. Chem. Soc.*, 1933, **55**, 3838; *A.*, 1933, 1167.

[7] G. Karagunis and G. Drikos, *Naturwiss.*, 1933, **33**, 607; *A.*, 1933, 1041.

A. Burawoy carried out an extensive examination of the relationship between light absorption and chemical constitution both in homopolar[8] and in heteropolar[9] compounds, and concluded that absorption is attributable either to radical-like chromophores such as the unsaturated atoms of free radicals (R-chromophores) or to conjugated systems (K-chromophores). The bands arising from these types are distinguished by markedly different persistence, and by the different bathochromic and hypsochromic effects of solvents and specific substituents. By examining the optical characters of mono-, di-, and tri-substituted coloured triarylmethyl ions in the light of these findings, it was concluded[10] that they are conjugated systems, and structural formulæ (I) and (II) were advanced, in

(I.) 

$$R_2N\cdot C_6H_4\cdot C{<}\begin{matrix} C_6H_4{:}\overset{+}{N}R_2 \\ | \\ C_6H_4\cdot NR_2 \end{matrix}$$

 (II.)

which each aryl group has a character different from that of the other two, in conformity with the optical differences found experimentally, but in pronounced disagreement with the carbonium and allied theories in which an identical function[11] is ascribed to each aryl residue. The work has been severely criticised, not always pertinently, by a number of workers;[12, 13, 14] the ensuing controversy cannot be profitably summarised, but Hantzsch and Burawoy still maintain in an unmodified form their original contentions.[15] On the other hand, the values[16] of the dissociation constants of the mono- and di-salts of *p*-amino-, *pp*′-diamino-, and *pp*′*p*″-triaminotriphenylcarbinol compared with those of the salts of the corresponding derivatives of triphenylmethane support the view that the coloured mono-salts are carbonium and not quinonoid.

Some semi-quantitative results of interest bearing on the relationship between radical formation and structure of ethanes have been obtained.[17] The relative ease of fission of the :C–C: bond in penta-arylethanes of the type $Ph_3C{\cdot}CHR_1R_2$ was compared by noting (a) the temperature at which they became coloured and (b) the rate of cleavage with hydriodic acid, sodium–potassium alloy, and sodium amalgam. It was found that the reactions of the penta-arylethanes represent reactions of a weakened :C–C: bond rather than those of free radicals. The strength of the bond is, however, greatly affected by the nature of the groups attached to its carbon atoms, and the ability to weaken it, in the order α-naphthyl > *p*-diphenylyl > anisyl > *p*-tolyl > phenyl > diphenylene, is essentially that representing the effect of groups in promoting the dissociation of hexa-arylethanes.

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[8] *Ber.*, 1930, **63**, 3155; *A.*, 1931, 144.

[9] *Idem, ibid.*, 1931, **64**, 462; *A.*, 1931, 544.

[10] *Idem, ibid.*, 1931, **64**, 1635; A. Hantzsch and A. Burawoy, *ibid.*, p. 1622; *A.*, 1931, 1052, 1051.

[11] See Ref. 25, pp. 1636—1637.

[12] W. Dilthey, *Ber.*, 1931, **64**, 1283; 1933, **66**, [*B*], 825; *J. pr. Chem.*, 1933, **136**, 61; W. Dilthey and R. Witzinger, *Ber.*, 1932, **65**, [*B*], 1329; *A.*, 1931, 955; 1933, 710, 391; 1932, 1127.

[13] P. Petrenko-Kritschenko, *Ber.*, 1933, **66**, [*B*], 1049, 1771; 1934, **67**, [*B*], 1349; *A.*, 1933, 1048; 1934, 186, 1000.

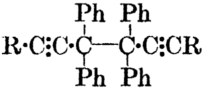
[14] I. Lifschitz, *Z. wiss. Phot.*, 1932, **32**, 131; *A.*, 1933, 1104.

[15] A. Burawoy, *Ber.*, 1932, **65**, [*B*], 949; A. Hantzsch and A. Burawoy, *ibid.*, 1934, **67**, [*B*], 788, 793; *A.*, 1932, 792; 1934, 769.

[16] P. Rumpf, *Compt. rend.*, 1934, **198**, 269; *A.*, 292.

Hexa-substituted ethanes containing acetylenic groups attached to the central carbon atoms show sensitivity towards oxygen, may be split under certain conditions by the action of alkali metals, and readily undergo rearrangement to give more stable hydrocarbons.[18] The ease with which rearrangement occurs appears to be dependent on the strength of the C–C ethane linkage: *e.g.*, none of the hexa(alkylacetylenyl)ethanes (III) undergo this rearrangement except under the influence of heat,[19] whereas all the tetra-aryldi(alkylacetylenyl)ethanes (IV) change to isomeric hydrocarbons at room temperature.[20]

(III.) $(R{\cdot}C{:}C)_3C{\cdot}C(C{:}CR)_3$



$$\mathrm{R{\cdot}C{:}C{\cdot}\underset{Ph}{\overset{Ph}{C}}—\underset{Ph}{\overset{Ph}{C}}{\cdot}C{:}CR}$$

(IV.)

A remarkable increase in the dissociation of hexa-arylethanes and tetra-aryldialkylethanes[21] occurs when a diphenylyl group is substituted for a phenyl group, and J. C. Y. Tsao and C. S. Marvel[22] set out to test critically the idea that the weakness of the central ethane link is the principal causative factor in this type of polyinene rearrangement by the preparation of tetrakisdiphenylyldi(*tert.*-butylacetylenyl)ethane (V). The reaction between tetramethylethylene dibromide and the sodio-compound (VI) at room temperature gave no evidence of the formation of (V), only a stable isomeride, $C_{62}H_{54}$, being produced. At − 80°, however, a solution

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[17] W. E. Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 2135, 3005; *A.*, 1933, 703, 943.

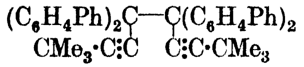
[18] M. T. Goebel and C. S. Marvel, *ibid.*, p. 3712; *A.*, 1933, 1153.

[19] P. L. Salzberg and C. S. Marvel, *ibid.*, 1928, **50**, 1737; I. L. Ozanne and C. S. Marvel, *ibid.*, 1930, **52**, 5267; D. W. Davis and C. S. Marvel, *ibid.*, 1931, **53**, 3840; *A.*, 1928, 988; 1931, 194, 1392.

[20] J. G. Stampfli and C. S. Marvel, *ibid.*, 1931, **53**, 4057; H. E. Munro and C. S. Marvel, *ibid.*, 1932, **54**, 4445; J. Harmon and C. S. Marvel, *ibid.*, 1933, **55**, 1716; *A.*, 1932, 50; 1933, 56, 605.

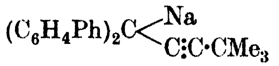
[21] J. B. Conant and R. F. Schultz, *ibid.*, 1933, **55**, 2098; *A.*, 1933, 703.

[22] *Ibid.*, p. 4709; *A.*, 1934, 63.



(V.)

$$\begin{matrix}(C_6H_4Ph)_2C & - & C(C_6H_4Ph)_2 \\ CMe_3\cdot C\vdots C & & C\vdots C\cdot CMe_3\end{matrix}$$

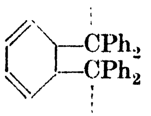


(VI.)

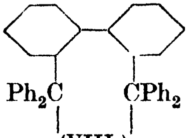
$$(C_6H_4Ph)_2C{<}^{Na}_{C\vdots C\cdot CMe_3}$$

was obtained which absorbed oxygen with avidity to produce bisdiphenylyl ketone. The properties of (V) are thus very similar to those of tetrakisdiphenylyldi-*tert.*-butylethane,[21] which is undeniably a free radical (75% dissoc. at 5°), and add considerable weight to the suggestion that rearrangements in the polyinenes occur through a weakening of the $\vdots C–C\vdots$ bond with the consequent transient formation of free radicals.

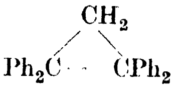
G. Wittig and M. Leo [23] advanced the hypothesis that the strain within a suitable carbon ring, assisted by sufficient loading of two of its carbon atoms, must enhance the tendency towards the rupture of the ring with the resultant formation of a *diradical*, and they successfully prepared radicals of the type $Ph_2\dot{C}\cdot C_6H_4\cdot[CH_2]_n\cdot C_6H_4\cdot\dot{C}Ph_2$, where $n = 1, 2, 3$, or 4.[24] The very broad absorption band in the spectra of the first two homologues corresponds to that of the monomeric trisdiphenylylmethyl, whereas in the third and fourth homologues it resembles that of the moderately dissociated hexaphenylethane. This marked difference in optical properties is in harmony with the expectations based on models: intramolecular union of the terminal radical valencies is impossible in the first two cases, but the ring strain allows such union for a diradical with a longer methylene bridge. Attempts to extend these researches with 1 : 1 : 2 : 2-tetraphenyl-*cyclo*butane and -*cyclo*butene were unsuccessful.[25] In the hope of obtaining the diradical (VII) the dipotassium derivative of ωωω′ω′-tetraphenyl-*o*-xylene was prepared,[26] but the elimination of the metal atom with tetramethylethylene dibromide, even at − 50°, yielded only 9 : 9 : 10-triphenyl-9 : 10-dihydroanthracene, and the action of oxygen on the potassium compound did not give a product with



(VII.)



(VIII.)



(IX.)

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[23] *Ber.*, 1928, **61**, 854; *A.*, 1928, 642.

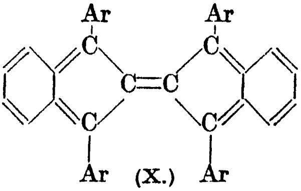
[24] *Ibid.*, 1929, **62**, 1405; *A.*, 1929, 921.

[25] G. Wittig and F. von Lupin, *ibid.*, 1928, **61**, 1627; *A.*, 1928, 1233.

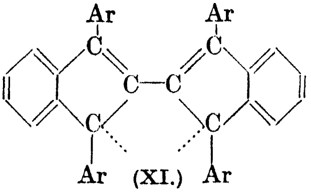
[26] G. Wittig and M. Leo, *ibid.*, 1931, **64**, 2395; *A.*, 1931, 1405.

the reactions of a radical peroxide. G. Wittig and H. Petri[27] then prepared 9:9:10:10-tetraphenyl-9:10-dihydrophenanthrene, hoping to get evidence of the formation of the radical (VIII): although the tetraphenyldihydrophenanthrene took up two atoms of potassium with an ease reminiscent of the reaction with triphenylmethyl, it was completely indifferent towards bromine even on heating. In its behaviour, therefore, it resembles tetraphenylethylene rather than hexaphenylethane. The synthesis of 1 : 1 : 2 : 2-tetraphenyl*cyclo*propane,[28] which might have shown weakness in the bond indicated by the dotted line in (IX), likewise gave a disappointing result, the product being colourless and extremely stable.

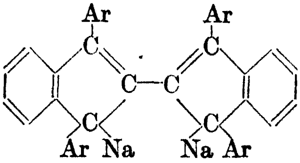
In a previous Report[29] it was pointed out that the most remarkable property of the rubrenes is their ability to absorb oxygen during irradiation; no oxidation occurs in the dark. This phenomenon has been explained[30, 31] on the assumption that the ordinary form of the molecule (X) tends to pass into the diradical form (XI) under certain conditions, for example, under the influence of light. This suggestion is in agreement with the easy addition of two atoms of sodium[32] to give (XII) and the reduction of the peroxide (XIII) to



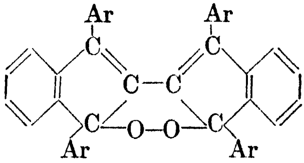
(X.)



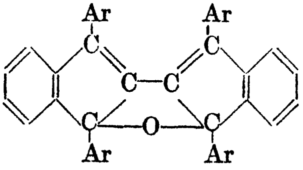
(XI.)



(XII.)



(XIII.)



(XIV.)

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[27] G. Wittig and H. Petri, *Annalen*, 1933, **505**, 17; *A.*, 1933, 944.

[28] G. Wittig and B. Obermann, *Ber.*, 1934, **67**, [*B*], 2053.

[29] *Ann. Reports*, 1933, **30**, 173.

[30] C. Dufraisse, *Bull. Soc. chim.*, 1933, [iv], **53**, 837; *Ber.*, 1934, **67**, [*B*], 1021, 2018; *A.*, 882.

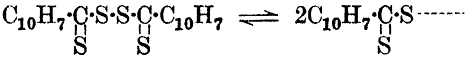
[31] A. Schönberg, *Ber.*, 1934, **67**, [*B*], 633, 1404; *A.*, 643, 997.

[32] C. Dufraisse, B. Masumoto, and R. Buret, *Bull. Soc. chim.*, 1932, [iv], **51**, 74; *A.*, 1932, 374.

give metrubrene, to which the constitution (XIV) had already been ascribed;[33] it also explains in a satisfactory manner the very small difference in the heats of formation of rubrene and oxyrubrene (XIII) pointed out in the previous Report,[29] since the heat of formation of the oxide from the diradical cannot be as large as that of an ordinary oxide ring or a carboxyl group.

A new type of radical containing univalent sulphur and analogous to the univalent oxygen compounds of R. Pummerer and S. Goldschmidt has been discovered.[34] H. Lecher[35] had early shown that diaryl disulphides obey Beer's law, have normal molecular weights, and are therefore non-dissociated. F. von Konek[36] came to the same conclusion regarding antipyryl disulphides. Schönberg has found, however, that solutions of di-α-thionaphthoyl disulphide (XV) and of diphenyl disulphide (XVI) do not obey Beer's law, in contrast with diphenylene disulphide (XVII), which is, nevertheless, markedly thermochromic. This behaviour is explained by dissociation into free radicals:

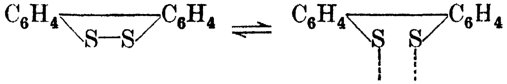
(XV.)



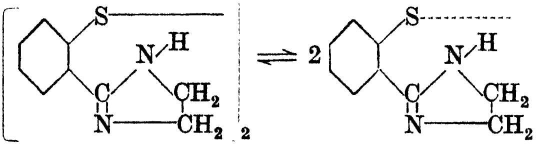
$$\mathrm{C_{10}H_7{\cdot}\underset{\underset{S}{\|}}{C}{\cdot}S{\cdot}S{\cdot}\underset{\underset{S}{\|}}{C}{\cdot}C_{10}H_7 \rightleftharpoons 2C_{10}H_7{\cdot}\underset{\underset{S}{\|}}{C}{\cdot}S\cdots\cdots}$$

(XVI.) $\mathrm{Ph{\cdot}S{\cdot}SPh \rightleftharpoons 2Ph{\cdot}S\cdots\cdots}$

(XVII.)



On these assumptions radical formation leads to an increase in the number of molecules in solution, and hence to a departure from Beer's law, only in the first two cases. The authors suggest that the departure observed for bis-*o*-dihydroglyoxalylphenyl disulphide[37] may also be due to radical formation:



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[33] C. Moureu, C. Dufraisse, and E. Enderlin, *Compt. rend.*, 1929, **188**, 1528; C. Dufraisse and M. Badoche, *ibid.*, 1930, **191**, 104; *A.*, 1929, 922; 1930, 1173.

[34] A. Schönberg, *Ber.*, 1932, **65**, [*B*], 1864; A. Schönberg, A. Stephenson, H. Kattschmitt, E. Petersen, and H. Schulten, *ibid.*, 1933, **66**, [*B*], 237; A. Schönberg, E. Rupp, and W. Gumlich, *ibid.*, p. 1932; A. Schönberg, *Naturwiss.*, 1933, **21**, 561; *Trans. Faraday Soc.*, 1934, **30**, 17; *A.*, 1933, 157, 291; 1934, 183; 1933, 1048.

[35] *Ber.*, 1915, **48**, 524, 1425; 1925, **58**, 417; *A.*, 1915, i, 532; 1916, i, 41; 1925, i, 390.

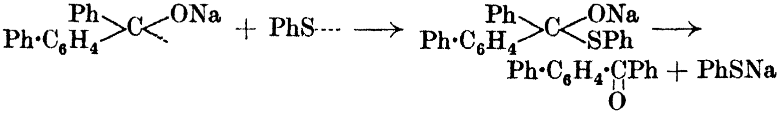
[36] *Ibid.*, 1920, **53**, 1666; *A.*, 1920, i, 880.

[37] W. E. McClelland and L. A. Warren, *J.*, 1930, 1096; *A.*, 1930, 928.

Apart from optical properties, the following evidence is adduced in favour of radical formation :

(*a*) (XV) and triphenylmethyl give $SPh_3\cdot CPh_3$;

(*b*) solutions of the sodio-derivative of phenyl diphenylyl ketone are almost instantaneously decolorised by (XV) and (XVI), thus :



$$\begin{matrix}Ph\\Ph\cdot C_6H_4\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}ONa\\ \cdot\end{matrix} + PhS\cdots \longrightarrow \begin{matrix}Ph\\Ph\cdot C_6H_4\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}ONa\\SPh\end{matrix} \longrightarrow Ph\cdot C_6H_4\cdot\underset{O}{\underset{\|}{C}}Ph + PhSNa$$

(*c*) (XVI) and diphenyldiazomethane yield $CPh_2(SPh)_2$ and nitrogen ;

(*d*) (XV) in boiling acetone or acetone–chloroform readily dissolves silver or zinc with the formation of compounds,

$$C_{10}H_7\cdot CS\cdot SAg,\tfrac{1}{2}C_5H_5N \text{ and } (C_{10}H_7\cdot CS\cdot S)_2Zn,C_5H_5N$$

(after recrystallisation from pyridine).

This remarkable reaction with free metals is, as the authors point out, without parallel in the ordinary chemistry of sulphur compounds and must be fundamentally connected with the chemistry of univalent sulphur. It will be interesting to see how far molecular weights and dipole moments will confirm the strong chemical and optical evidence of the true radical nature of these "*thiyls.*"

Experiments on the reactions and structure of metal ketyls have recently been made. The observation of Schlenk and his co-workers that hydrolysis of these compounds gives, not pinacols, but a mixture of ketone and hydrol has always been held to favour their unimolecular structure ($2R_2C\cdot ONa \xrightarrow{H_2O} 2R_2C\cdot OH \longrightarrow R_2CO + R_2CH\cdot OH$) and W. Schlenk's view that they contain tervalent carbon has been generally preferred to Schmidlin's formulation,[38] $R_2C{:}O\cdots\cdots Na$, against which additional evidence has been recently adduced.[39] In 1927, M. Gomberg and W. E. Bachmann [40] showed that aromatic ketones react with a mixture of magnesium and magnesium iodide to yield iodomagnesium pinacolates, $R_2C(OMgI)\cdot CR_2(OMgI)$, which, although colourless in the solid state, give coloured solutions ; the conclusion that they dissociate to a slight extent to give iodomagnesium ketyl radicals was confirmed by the reactions of the solutions towards iodine and oxygen. That the dissociation was slight was inferred from their hydrolysis, in which a quantitative yield of pinacol was obtained, but no ketone or hydrol. W. E. Bachmann [41] then inferred that the absence of pinacols in the hydrolysis of alkali ketyls is due to the very rapid hydrolysis of pinacol in the presence of even a small amount of strong alkali solution; when the hydrolysis was carried out in acetic acid solution, pinacols in yields as high as 95% were obtained, and he concluded that the " sodium derivatives of ketones . . . are not mono-molecular free radicals, but sodium pinacolates or equilibrium mixtures of sodium ketyl and pinacolate in which the equilibrium is nearly entirely in favour of the sodium pinacolate." This is hardly satisfactory in view of the molecular-weight determinations of W. Schlenk and A. Thal,[42] which indicate that potassium phenyl *p*-diphenylyl ketyl is wholly unimolecular, and S. Sugden's important finding[43] that this compound, and also benzophenone potassium, in dioxan solution are paramagnetic ($\chi\mu = 1080$ and 1050 respectively), and are therefore largely present as the monomeric species. Furthermore, the hydrolysis[44] of sodium benzpinacolate by ammonium bromide or chloride in liquid ammonia yields only 10·9% of benzpinacol, a result which cannot be explained by decomposition of the pinacol either by the ammonium salt solutions or by excess of the sodium compounds.[44] It would thus appear that the nature of the products of hydrolysis of metal ketyls is greatly dependent on the conditions of the experiment, and does not give accurate information concerning the molecular complexity of the original ketyl.

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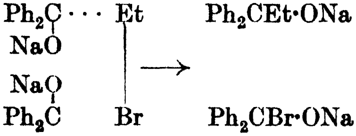
[38] "Das Triphenylmethyl," Stuttgart, 1914, p. 186.

[39] C. B. Wooster, *J. Amer. Chem. Soc.*, 1932, **54**, 834; *A.*, 1932, 386.

[40] *Ibid.*, 1927, **49**, 236; *A.*, 1927, 245.

[41] *Ibid.*, 1933, **55**, 1179, 2827; *A.*, 1933, 505, 952.

The reaction between metal ketyls and alkyl halides proceeds according to W. Schlenk and T. Weickel[45] by a cleavage of the alkyl halide molecule according to the scheme



$$\begin{array}{ll} Ph_2C\cdots & Et \\ NaO & \\ NaO & \\ Ph_2C & Br \end{array} \longrightarrow \begin{array}{l} Ph_2CEt{\cdot}ONa \\ \\ \\ Ph_2CBr{\cdot}ONa \end{array} \qquad (A)$$

followed by

$$Ph_2CBr{\cdot}ONa \longrightarrow Ph_2CO + NaBr \qquad (B)$$

Slow addition of ethyl bromide to sodium benzophenone leads to the formation of benzophenone in 99% yield in accordance with equations (A) and (B), but very rapid addition of excess of ethyl bromide gives only a 20% yield.[46] These results do not confirm the mechanism already outlined, and are best understood by the postulation of two successive reactions :

[42] *Ber.*, 1913, **46**, 2840; *A.*, 1913, i, 1205.

[43] *Trans. Faraday Soc.*, 1934, **30**, 23; *A.*, 1933, 1232.

[44] C. B. Wooster and W. E. Holland, *J. Amer. Chem. Soc.*, 1934, **56**, 2436.

[45] *Ber.*, 1911, **44**, 1182; *A.*, 1911, i, 545.

[46] C. B. Bushnell and W. E. Holland, *J. Amer. Chem. Soc.*, 1934, **56**, 2438.

$C_{13}H_{10}\cdot ONa + C_2H_5Br = NaBr + C_{15}H_{15}O$ (C)
$C_{15}H_{15}O + C_{13}H_{10}\cdot ONa = (C_6H_5)_2CO + Ph_2CEt\cdot ONa$ (D)

The rapid addition of ethyl bromide may then be regarded as consuming the ketyl so rapidly by reaction (C) that reaction (D) is largely eliminated.

The formation of metal ketyls has hitherto been regarded as a property peculiar to aromatic ketones, but A. E. Favorsky and J. N. Nazarov [47] have now prepared ketyls of the aliphatic series. Sodium reacts with di-*tert.*-butyl ketone to give a deep red ketyl, the solution of which is decolorised on exposure to air with the appearance of reactions for hydrogen peroxide. Unlike the aromatic ketyls, sodium di-*tert.*-butyl ketyl passes into the dimeric form when kept for several days either dry or in ethereal solution. *iso*Propyl *tert.*-butyl ketone likewise reacts with sodium to give a ketyl. The interaction of aceto-, propio-, butyro-, or *iso*butyro-phenone with sodium [48] produces a red colour, which disappears after a few days with the formation of a pinacol. ω-Diethyltrimethyl-, ω-dimethylethyl-, ω-methyldiethyl-, and ω-triethyl-acetophenone afford stable crystalline ketyls under similar conditions, indicating that branched aliphatic chains favour their formation. This result is reminiscent of those obtained in other parts of the free-radical field, *e.g.*, the superior dissociation of tetrakisdiphenylyldi-*tert.*-butylethane in comparison with the analogous products with unbranched chains.[21]

The formation of free radicals as intermediates in a number of reactions was referred to in a previous Report.[49] The absence of free radicals [50] in the thermal decomposition of diacyl peroxides has been confirmed,[51] and the decomposition of triphenylmethyl azo-compounds,[52] $Ph_3C\cdot N\colon NR$, appears to proceed through CPh_3 and R, which rapidly react with other molecules to give stable end-products. When triphenylmethyl bromide in *cyclo*hexane solution is irradiated with sunlight,[53] it is converted into a peroxide and unidentified products, and the absorption spectrum indicates the intermediate formation of triphenylmethyl. It was shown some years ago[54] that halochromic salts of triphenylcarbinol are reduced by powerful agents in appropriate solutions with the formation of the corresponding free radical. This work has been recently extended[55] to the reduction of malachite-green, *p*-dimethylaminobenzhydrol, and *p*-dimethylaminotriphenylcarbinol. By varying the conditions of reduction, three different products were isolated from the last-named compound, *viz.*, *s.*-bis-(*p*-dimethylaminotriphenyl)ethane, *p*-dimethylaminotriphenylmethane, and a compound, $C_{42}H_{40}N_2$, analogous in constitution to *p*-benzhydryltetraphenylmethane (Tschitschibabin compound). These results are best understood if the radical *p*-dimethylaminotriphenylmethyl ($R\cdot$) occurs as an intermediate, followed by the changes :

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[47] *Compt. rend.*, 1933, **196**, 1229; *A.*, 1933, 702; *Bull. Acad. Sci. U.R.S.S.*, 1933, 1309; *C.A.*, 1934, **27**, 2673; *Bull. Soc. chim.*, 1934, [v], **1**, 46; *A.*, 758.

[48] *Idem, Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **1**, 325; *A.*, 654.

[49] *Ann. Reports*, 1930, **27**, 127.

[50] H. Wieland, S. Schapero, and H. H. Metzger, *Annalen*, 1934, **513**, 93; *A.*, 1215.

[51] *Ibid.*, 1930, **480**, 157; *A.*, 1930, 911.

[52] H. Wieland, K. Heymann, T. Tsatsas, D. Juchum, G. Varvoglis, G. Labriola, O. Dobbelstein, and H. S. Boyd-Barrett, *ibid.*, 1934, **514**, 145; *A.*, 1935, 77.

[53] J. O. Halford and L. C. Anderson, *Proc. Nat. Acad. Sci.*, 1933, **19**, 759; *A.*, 1933, 1041.

$2R\cdot \rightleftharpoons R\cdot R$ (the ethane), a reaction which is fast, reversible or irreversible according to the nature of $R\cdot$,

$2R\cdot + H^+ \longrightarrow RH$ (the methane) $+ R^+$, irreversible,

$2R\cdot \longrightarrow R_2$ (the Tschitschibabin compound), irreversible and catalysed by acids.

Free radicals containing tervalent carbon combine with quinones, and with other free radicals containing bivalent nitrogen. J. B. Conant and H. W. Scherp[56] find that triphenylmethyl combines with isoprene and with dimethylbutadienes, addition occurring in the 1 : 4-positions to yield respectively $\alpha\alpha\alpha\xi\xi\xi$-hexaphenyl-$\gamma$-methyl-$\Delta^{\gamma}$-hexene and a hydrocarbon $C_{44}H_{40}$. Phenylxanthyl and benzylxanthyl also combine with dienes, pyrrole, and maleic anhydride.[57] With isoprene, reaction occurs more slowly than with triphenylmethyl, and since phenylxanthyl is more dissociated than triphenylmethyl, and benzylxanthyl much more so, it is evident that the reaction does not primarily depend on the degree of dissociation of the radical involved. The reactions between triphenylmethyl and ethers, esters, and acetone have also been examined.[58]

Short Life.—It is known that the free unexcited hydroxyl radical can exist in thermodynamical equilibrium with water vapour and its decomposition products at high temperatures,[59] and although its life is so short that it does not appear to be removable from a discharge through water vapour,[60, 61] yet the absence of its typical absorption bands from the spectra of systems wherein its presence might have been reasonably expected [60, 62a] has been very puzzling. O. Oldenberg [63] now suggests that failure to observe hydroxyl in absorption is probably due to the use of small spectrographs, since extremely high resolving power is required to observe a faint and sharp *absorption* line, contrary to the corresponding problem in *emission*. By the aid of a 21-foot grating, the absorption spectrum of hydroxyl could be seen in an uninterrupted discharge, provided that an intense continuous background was used, and that a modification of H. B. Dorgelo's method,[64] without restriction after the interruption of the discharge, was employed (compare, however, ref. 62*b*).

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[54] J. B. Conant, L. F. Small, and B. S. Taylor, *J. Amer. Chem. Soc.*, 1925, **47**, 1959; *A.*, 1925, ii, 874.

[55] J. B. Conant and N. M. Bigelow, *ibid.*, 1931, **53**, 676; *A.*, 1931, 480.

[56] *Ibid.*, 1931, **53**, 1941; *A.*, 1931, 1043.

[57] J. B. Conant and B. F. Chow, *ibid.*, 1933, **55**, 3475; *A.*, 1933, 1041.

[58] A. A. Morton and L. V. Peakes, *ibid.*, p. 2449; *A.*, 1933, 815.

[59] K. F. Bonhoeffer and H. Reichardt, *Z. physikal. Chem.*, 1928, **139**, 75; *A.*, 1928, 1188.

The methyl radicals [65] resulting from the thermal decomposition at low pressures of butane, acetone, or diethyl ether react with a mirror of tellurium at 100—200° to produce dimethyl ditelluride, $Te_2(CH_3)_2$, a deep red, comparatively stable liquid, and it is suggested that metallic tellurium is almost the ideal reagent for use in the identification of methyl radicals. It is doubtful, however, whether it can surpass F. A. Paneth's antimony cacodyl.[66] When diazomethane [67] is carried in the vapour of ether or butane at low pressures through a quartz tube heated below 550°, the products, consisting partly of short-lived radicals, remove mirrors of tellurium, selenium, antimony, and arsenic, but leave unattacked zinc, cadmium, thallium, lead, and bismuth. When tellurium was used, a red involatile solid, insoluble in the usual solvents, was deposited just behind the original position of the metal mirror; on analysis it gave figures in fair agreement with the empirical formula CH_2Te. The red product was therefore presumed to be polymerised telluroformaldehyde, resulting from the action of methylene radicals, CH_2, on the metal. The properties of this polymeride led the authors to doubt whether L. Belchetz [68] ever had methylene radicals, because his product, the result of the reaction between tellurium and the products of dissociation of methane on a platinum filament,

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[60] K. F. Bonhoeffer and T. G. Pearson, *Z. physikal. Chem.*, 1931, **14**, [*B*], 1; *A.*, 1931, 1215.

[61] E. M. Stoddart, *Phil. Mag.*, 1934, [vii], **18**, 407; *A.*, 1183.

[62] (*a*) H. Geib and P. Harteck, *Trans. Faraday Soc.*, 1934, **30**, 139; *A.*, 1933, 1254. (*b*) *Idem*, *Z. physikal. Chem.*, 1934, **170**, 1.

[63] *J. Chem. Physics*, 1934, **2**, 713; *A.*, 1286.

[64] *Z. Physik*, 1925, **34**, 766; *A.*, 1926, 101.

[65] F. O. Rice and A. L. Glasebrook, *J. Amer. Chem. Soc.*, 1934, **56**, 2472.

[66] *Trans. Faraday Soc.*, 1934, **30**, 179; *A.*, 1933, 1138.

[67] F. O. Rice and A. L. Glasebrook, *J. Amer. Chem. Soc.*, 1934, **56**, 2381; 1933, **55**, 4329; *A.*, 1933, 1269.

[68] *Trans. Faraday Soc.*, 1934, **30**, 170; *A.*, 1933, 1270.

was volatile enough to pass from the mirror at which it was formed into a liquid-air trap. Belchetz, however, used cold mirrors, which may account for the difference. The products of diazomethane,[67] decomposed in the quartz tube above 550°, when allowed to react with mercury, gave only $HgMe_2$, identified as HgMeI after reaction with iodine, and the authors hold this for additional evidence against Belchetz's findings, especially since in the thermal dissociation of methane, ethane, propane, and butane [69] methyl groups alone were detected. Again, attention should be drawn to the possibility of differences arising through the very different experimental conditions : the passage of methane over a platinum filament in the one case, and through a quartz tube some centimetres long in the other.

J. A. Leermakers [70] decomposed azomethane above 475° and was able to remove lead mirrors with the fragments, and F. O. Rice and B. L. Evering [71] obtained similar evidence of free radicals in the products from azomethane and azo*iso*propane, and held that *iso*propyl radicals might be present.

Attempts to prepare the ethylidene radical [72] $CH_3{\cdot}CH$ through the dissociation of diazoethane, $CH_3{\cdot}CH{:}N{:}N$, were unsuccessful, and it was concluded that, if it is formed, it must be of very short life, and undergo the rearrangement $CH_3{\cdot}CH \longrightarrow CH_2{:}CH_2$ with great ease.

The probable formation of CH_2 during the photolysis of keten [73] has been confirmed,[74] attention has been drawn to the possible existence of the same radical during the Schumann excitation of *cyclo*pentanone and *cyclo*hexanone,[75] and the emission spectra of OH and CN have been observed [76] accompanying the photo-dissociation of more complex molecules by light in the same spectral region :

$$h\nu + H_2O \longrightarrow H + OH^*$$
$$h\nu + CH_3{\cdot}OH \longrightarrow CH_3 + OH^*$$
$$h\nu + CH_3{\cdot}CN \longrightarrow CH_3 + CN^*$$

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[69] F. O. Rice, *J. Amer. Chem. Soc.*, 1934, **56**, 488; F. O. Rice and B. L. Evering, *ibid.*, p. 2105; *A.*, 388, 1341.

[70] *Ibid.*, 1933, **55**, 3499; *A.*, 1933, 1039.

[71] *Ibid.*, p. 3898; *A.*, 1933, 1149.

[72] F. O. Rice and A. L. Glasebrook, *ibid.*, 1934, **56**, 741; *A.*, 508.

[73] R. G. W. Norrish, H. G. Crone, and (Miss) O. Saltmarsh, *J.*, 1933, 1533; *A.*, 1934, 156.

[74] W. F. Ross and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 1112; *A.*, 740.

[75] G. Scheibe and H. Grieneisen, *Z. physikal. Chem.*, 1934, **25**, [*B*], 52; E. P. Carr and H. Stucklen, *Helv. Physica Acta*, 1933, **6**, 261; *Chem. Zentr.*, 1934, ii, 566, 565.

[76] A. Terenin and H. Neujmin, *Nature*, 1934, **134**, 255; *A.*, 1079.

It has also been suggested [77] that the radical C_2H may be present during the photolysis of acetylene, and that free radicals occur during the photo-dissociation of dimethylzinc, dimethylmercury, and tetraethyl-lead.[78]

R. G. W. Norrish [79] proposed, as a result of a large number of experiments,[80] that there is an essential difference in the photo-dissociation of ketones and aldehydes, free radicals participating in the former reactions, but not necessarily in the latter. These views have been widely discussed and criticised.[81, 82, 83] It has now been shown [84] that, whereas free alkyl radicals may be isolated from the products of photolysis of certain ketones, their presence cannot be detected during the decomposition of acetaldehyde or propaldehyde under identical conditions, so that a difference in the two mechanisms exists. If free radicals are formed from aldehydes, as J. A. Leermakers' experiments [83] imply, they must be removed very rapidly indeed as a result of secondary reactions.

The hypothetical existence of radicals in the thermal dissociation of a number of organic compounds [85] has received some confirmation from recent researches [86] in which reactions have been induced by the introduction of methyl radicals from photolysing acetone.

The action of an electric discharge (500-watt transformer giving 10 k.-volts) on *n*-butane, *n*-heptane, ethylene, methyl alcohol, ethyl alcohol, acetaldehyde, acetic acid or acetone [87] gave short-lived products capable of removing mirrors of antimony or lead, but not those of cadmium or zinc. This strange behaviour cannot be accounted for by the presence of alkyl radicals or atomic hydrogen,[88] unless their mutual presence induces reactions which do not occur with either individual alone.[89] T. G. P.

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[77] S. C. Lind and R. Livingston, *J. Amer. Chem. Soc.*, 1934, **56**, 1550.

[78] A. Terenin, *J. Chem. Physics*, 1934, **2**, 441; *A.*, 940.

[79] *Trans. Faraday Soc.*, 1934, **30**, 107; *A.*, 1933, 1256.

[80] See bibliography in Ref. 84.

[81] *Trans. Faraday Soc.*, 1934, **30**, 118.

[82] *Proc. Roy. Soc.*, 1934, [*A*], **146**, 239.

[83] *J. Amer. Chem. Soc.*, 1934, **56**, 1537, 1899; *A.*, 976, 1184.

[84] T. G. Pearson, *J.*, 1934, 1718.

[85] F. O. Rice and K. Hertzfeld, *J. Amer. Chem. Soc.*, 1934, **56**, 284; *A.*, 369.

[86] D. V. Sickman and A. O. Allen, *ibid.*, p. 1251; *A.*, 758.

[87] F. O. Rice and F. R. Whalley, *ibid.*, p. 1311; *A.*, 863.

[88] T. G. Pearson, P. L. Robinson, and E. M. Stoddart, *Proc. Roy. Soc.*, 1933, [*A*], **142**, 275; *A.*, 1933, 1257.

[89] P. Harteck, *Trans. Faraday Soc.*, 1934, **30**, 140; *A.*, 1933, 1254.

PART III.—HETEROCYCLIC DIVISION.

Substitution in Diphenylene Oxide and Diphenylene Sulphide.

WHEN diphenylene oxide is brominated, first the 3-bromo- and then the 3 : 6-dibromo-derivative is formed.[1] On the other hand, when diphenylene oxide is nitrated, the 2-mononitro-compound is produced, and this, on further nitration, gives the 2 : 6-dinitro-derivative.[2] Similarly, bromination of 2-nitrodiphenylene oxide gives rise to the 6-bromo-2-nitro-compound.[3] Later work [4] confirmed the foregoing results, and moreover it was shown that nitration of 2-bromo-diphenylene oxide produced the 2-bromo-6-nitro-derivative. Yet sulphonation of diphenylene oxide takes place in position 3, and disulphonation in positions 3 and 6.[5] An explanation has been suggested by R. Robinson (see ref. 2) for the fact that bromination and nitration take place in two different positions, but so far no explanation has been offered for the contrast between diphenylene oxide and diphenylene sulphide in their substitution reactions. C. Courtot and C. Pomonis [6] concluded that diphenylene sulphide underwent 2-mononitration and 2 : 7-dinitration, and C. Courtot, L. Nicolas, and T. H. Liang [7] found that bromination and dibromination took place in the 2- and the 2 : 7-positions. C. Courtot and Chaix [8] then showed that the dibromodiphenylenesulphone obtained by oxidation of dibromodiphenylene sulphide was converted into sodium 3 : 3′-dibromodiphenyl-2-sulphonate, the constitution of which was established by the fact that 3 : 3′-dibromodiphenyl was formed when the sulphonate was heated under pressure with hydrobromic acid.

This necessitated a revision of the previous conclusions, and in a recent paper [9] C. Courtot and I. Kelner state that halogenation, nitration, sulphonation, etc., all occur in the position para (or ortho) to the sulphur atom.

The outstanding result of the above work is, therefore, that the sulphur atom exerts a more powerful orienting influence in diphenylene sulphide than oxygen exerts in the oxide.

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[1] H. McCombie, W. G. Macmillan, and H. A. Scarborough, *J.*, 1931, 529; *A.*, 1931, 616.

[2] N. M. Cullinane, *J.*, 1932, 2365; *A.*, 1932, 1140.

[3] N. M. Cullinane, H. G. Davey, and H. J. H. Padfield, *J.*, 1934, 716; *A.*, 779.

[4] H. Gilman, G. E. Brown, W. G. Bywaters, and W. H. Kirkpatrick, *J. Amer. Chem. Soc.*, 1934, **56**, 2473; *A.*, 1935, 91.

[5] H. Gilman, E. W. Smith, and H. J. Oatfield, *ibid.*, p. 1412; *A.*, 899; H. Gilman and R. V. Young, *ibid.*, p. 1415; *A.*, 899.

[6] *Compt. rend.*, 1926, **182**, 893, 931; *A.*, 1926, 605, 620.

[7] *Ibid.*, 1928, **186**, 1624; *A.*, 1928, 896.

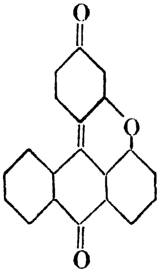
[8] *Ibid.*, 1931, **192**, 1667; *A.*, 1931, 1406.

[9] *Ibid.*, 1934, **198**, 2003; *A.*, 900.

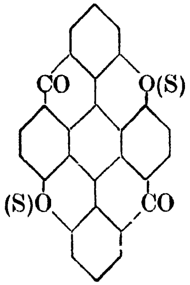
Oxygen Ring Compounds.

Miscellaneous.—F. E. King [10] has investigated the synthesis of coeroxonones, *e.g.*, of coeroxonone-3 : 9 (I). R. Scholl, O. Böttger, and L. Wanka [11] have prepared the oxygen and sulphur analogues, dioxido- and disulphido-*hetero*coerdianthrone (II), of antidiperidibenzcoronene.

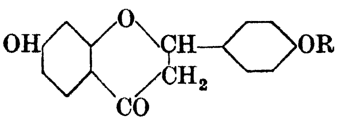
(I.)



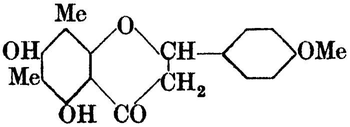
(II.)



Flavan Derivatives.—Although flavanones derived from phloroglucinol are common, butin was the only one known to be derived from resorcinol until J. Shinoda and S. Ueeda [12] obtained liquiritigenin (III; R = H) from liquorice root (*Glycyrrhiza glabra* L.). Liquiritigenin was obtained by hydrolysing liquiritin (III; R = glucosidyl), and its constitution was established by usual methods of degradation and synthesis.



(III.)



(IV.)

S. Fujise and T. Nishi [13] found that synthetic demethoxymatteucinol slightly depressed the melting point of the material of natural origin, although the chemical identity of the two compounds seemed quite definite. It is now shown [14] that demethoxymatteucinol and matteucinol (IV) itself are optically active and, when warmed with concentrated sulphuric acid, undergo racemisation to produce compounds the melting points of which are not depressed by the original synthetic materials. This is the first recorded example of an optically active flavanone.

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[10] *J.*, 1934, 1064; *A.*, 1108.

[11] *Ber.*, 1934, **67**, [*B*], 599; *A.*, 661.

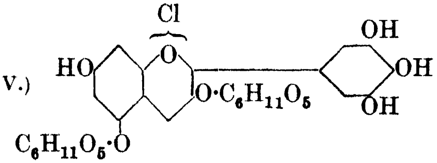
[12] *Ibid.*, p. 434; *A.*, 513.

[13] *Ibid.*, 1933, **66**, [*B*], 929; *A.*, 1933, 832.

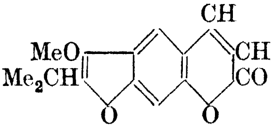
[14] S. Fujise and T. Kubota, *ibid.*, 1934, **67**, [*B*], 1905; *A.*, 1935, 31.

Anthocyanins.—R. Robinson [15] has given a valuable survey of synthetical methods in this series. 5-Glucosidylapigeninidin, believed to be identical with the natural gesnerin, has been synthesised,[16] as has also delphin (*O*-3 : 5-diglucosidyldelphinidin chloride; V), an anthocyanin present in *Salvia patens*.[17]

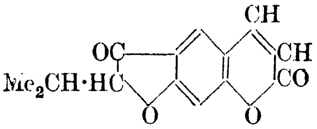
(V.)



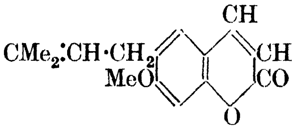
Fish Poisons.—In these Reports for 1932 (p. 191) reference was made to preliminary work [18] on the constitutions of peucedanin and oreoselone. These have now been elucidated.[19] The presence of the coumarin ring in oreoselone was definitely proved by reduction, followed by alkali fusion, 7-hydroxydihydrocoumarin then being formed. A further informative result was that α-hydroxy*iso*valeric acid was produced by acid permanganate oxidation of oreoselone. This substance is therefore (VII), and peucedanin is (VI).



(VI.)



(VII.)



(VIII.)

Osan [20] gave the name imperatorin to the crude mixture he extracted from *Imperatoria Ostruthium* (masterwort). Seven components have been recognised. J. Herzog and D. Krohn [21] characterised oxypeucedanin, ostruthol, osthol, and ostruthin; and osthin was isolated by Merck.[22] Two further individuals, imperatorin [23] and *iso*imperatorin,[24] have recently been isolated. The preliminary work [21] on osthol was extended by A. Butenandt and A. Marten,[25] who obtained acetone and an acid (ostholic) by oxidation and concluded that osthol was (VIII). Later work by E. Späth and E. Pesta [26] showed that the side chain was in position 8. Tetrahydro-osthol, when oxidised under different conditions, gave either succinic acid (revealing the coumarin structure) or *iso*hexoic acid (showing the presence of a 5-carbon side chain). Decarboxylation of ostholic acid gave a methoxymethylcoumarin, oxidation of which yielded 2-hydroxy-6-methoxy-*m*-toluic acid (IX). The last series of changes is explained as follows, osthol being (X):

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[15] *Ber.*, 1934, **67**, [*A*], 85.

[16] (Mrs.) G. M. Robinson, R. Robinson, and A. R. Todd, *J.*, 1934, 809; *A.*, 899.

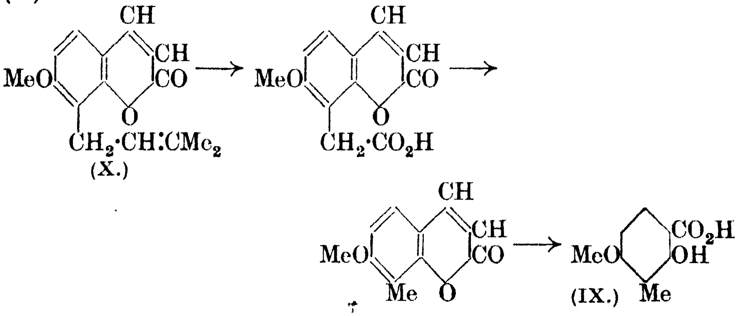
[17] (Miss) T. M. Reynolds, R. Robinson, and (Miss) R. Scott-Moncrieff, *ibid.*, p. 1235; *A.*, 1107.

[18] E. Späth, K. Klager, and C. Schlösser, *Ber.*, 1931, **64**, [*B*], 2203; *A.*, 1931, 1298.

[19] E. Späth and K. Klager, *ibid.*, 1933, **66**, [*B*], 749; *A.*, 1933, 614.

[20] *Arch. Pharm.*, 1831, **37**, 346.

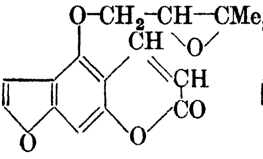
[21] *Ibid.*, 1909, **247**, 553; *A.*, 1910, i, 124.



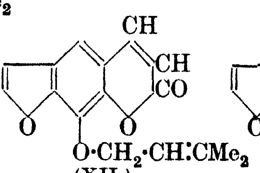
(X.)

(IX.)

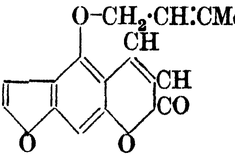
Oxypeucedanin was at first thought [21] to contain a methylenedioxy-group, but was subsequently shown [27] to be closely related to bergapten: alkali fusion gave phloroglucinol; reduction gave a dihydro-derivative, which afforded succinic acid when oxidised;



(XI.)



(XII.)



(XIII.)

alkaline hydrogen peroxide gave furan-2 : 3-dicarboxylic acid. Finally, by hydrolysis (acetic and sulphuric acids) bergapten was isolated, and oxypeucedanin shown to be (XI). Imperatorin[23] and *iso*imperatorin[24] were similarly shown to be, respectively, (XII) and (XIII).

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[22] *Gesch.-Ber.*, 1895, Jan. 8.

[23] E. Späth and H. Holzen, *Ber.*, 1933, **66**, [*B*], 1137; *A.*, 1933, 1056.

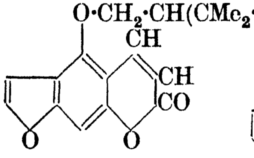
[24] E. Späth and L. Kahovec, *ibid.*, p. 1146; *A.*, 1933, 1056.

[25] *Annalen*, 1932, **495**, 187; *A.*, 1932, 751.

[26] *Ber.*, 1933, **66**, [*B*], 754; *A.*, 1933, 614.

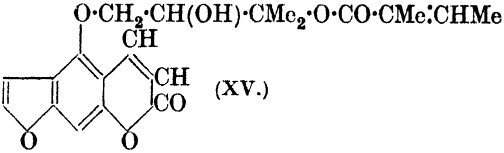
[27] E. Späth and K. Klager, *ibid.*, p. 914; *A.*, 1933, 833.

For ostruthol, E. Späth and A. Freiherr von Christiani[28] propose one of the two structures (XIV) and (XV), with a preference for (XIV).



$O{\cdot}CH_2{\cdot}CH(CMe_2{\cdot}OH){\cdot}O{\cdot}CO{\cdot}CMe{:}CHMe$

(XIV.)



$O{\cdot}CH_2{\cdot}CH(OH){\cdot}CMe_2{\cdot}O{\cdot}CO{\cdot}CMe{:}CHMe$

(XV.)

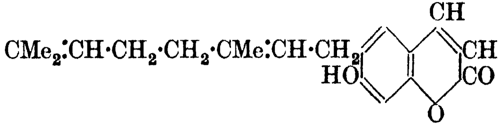
An interesting point is that ostruthol is the angelic ester of optically active oxypeucedanin hydrate, whereas the oxypeucedanin occurring *in the same plant* is the ethylene oxide of optically inactive oxypeucedanin hydrate.

Ostruthin, which A. Butenandt and A. Marten[25] regarded as a 6-substituted 5-hydroxycoumarin, $C_{18}H_{20}O_3$, was found by E. Späth and K. Klager[29] to have the formula $C_{19}H_{22}O_3$. The latter authors showed that the hydroxyl group was in position 5. Oxidation of hexahydro-ostruthin produced a C_{11} acid, and oxidation of ostruthin methyl ether gave acetone, an aldehyde, and β-methyl-Δ^{β}-hepten-ζ-one, showing the C_{11} acid to be

$$CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H.$$

This acid has been synthesised from tetrahydrogeranyl bromide. Ostruthin is therefore (XVI).

(XVI.)



$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2$

Angelica root contains three substances, osthol, sitosterol, and angelicin. The last, when oxidised with alkaline hydrogen peroxide, gives furan-2 : 3-dicarboxylic acid, and permanganate oxidation in pyridine solution, followed by decarboxylation of the product, affords umbelliferone. This suggests[30] that angelicin is (XVII). Methylation of osthol in alkaline solution, followed by oxidation of the product, gave an acid, characterised as the anilide, which was identical with the anilide of an acid obtained by submitting angelicin to similar treatment : this establishes (XVII) as the constitution of angelicin, which was synthesised[31] as follows: condensation of bromoacetal with the sodium salt of 7-hydroxycoumarin gave (XVIII), which was caused to undergo ring-closure, (XVII) being obtained.

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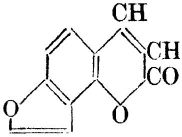
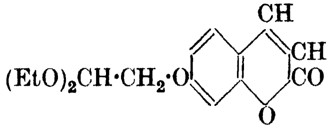
[28] *Ber.*, 1933, **66**, [*B*], 1150; *A.*, 1933, 1056.

[29] *Ibid.*, 1934, **67**, [*B*], 859; *A.*, 779.

[30] E. Späth and O. Pesta, *ibid.*, p. 853; *A.*, 779.

(XVII.)





(XVIII.)

H. L. Haller and F. Acree[32] have synthesised 7-methoxy-8-*iso*amylcoumarin (dihydro-osthol) from tetrahydrotubaic acid.

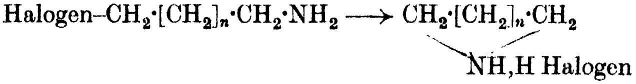
Nitrogen Ring Compounds.

Cyclic Imines.—A. Müller and A. Sauerwald,[33] by treating αζ-dibromohexane in alcoholic solution with two molecules of sodium ethoxide and one molecule of *p*-toluenesulphonamide, obtained a 25% yield of *N*-*p*-toluenesulphonylhexamethyleneimine. K. Ziegler and P. Orth,[34] in continuation of Ziegler's kinetic studies on ring closure,[35] have shown that yields up to 60% may be obtained when the two reactions proceed separately. The first reaction, $C_6H_4Me\cdot SO_2\cdot NHNa + Br\cdot[CH_2]_6\cdot Br = C_6H_4Me\cdot SO_2\cdot NH\cdot[CH_2]_6\cdot Br + NaBr$, is rapid and free from side reactions when half a molecular proportion of sodium butoxide is added slowly to a boiling solution of *p*-toluenesulphonamide and dibromohexane in butyl alcohol. The second reaction,

$$C_6H_4Me\cdot SO_2\cdot NNa\cdot[CH_2]_6\cdot Br = C_6H_4Me\cdot SO_2\cdot N[CH_2]_6 + NaBr,$$

proceeds to the extent of 75% when equivalent quantities of sodium butoxide and the bromosulphonamide are added gradually to benzyl alcohol kept at 170°.

H. Freundlich and H. Kroepelin[36] summarised the results obtained during the period 1911—1926 by Freundlich and his co-workers, and these are now discussed[37] in connexion with the velocity of the change:



$$\text{Halogen–}CH_2\cdot[CH_2]_n\cdot CH_2\cdot NH_2 \longrightarrow \underset{\text{NH,H Halogen}}{CH_2\cdot[CH_2]_n\cdot CH_2}$$

The reaction was of the first order, had the characteristic high temperature coefficient, and was not affected by excess of alkali, or by the presence of neutral salts. The constants for the reaction at 25° were:

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[31] E. Späth and M. Pailer, *Ber.*, 1934, **67**, [*B*], 1212; *A.*, 899.

[32] *J. Amer. Chem. Soc.*, 1934, **56**, 1389; *A.*, 899.

[33] *Monatsh.*, 1927, **48**, 727; *A.*, 1928, 277.

[34] *Ber.*, 1933, **66**, [*B*], 1867; *A.*, 1934, 195.

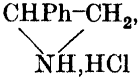
[35] K. Ziegler, H. Eberle, and H. Ohlinger, *Annalen*, 1933, **504**, 94; *A.*, 1933, 195.

[36] *Z. physikal. Chem.*, 1926, **122**, 39; *A.*, 1926, 1010.

[37] H. Freundlich and G. Salomon, *Ber.*, 1933, **66**, [*B*], 355; *A.*, 1933, 399.

	k.		*k*.
β-Bromoethylamine	36×10^{-3}	*ε*-Bromoamylamine.........	5×10^{-1}
γ-Bromopropylamine ...	5×10^{-4}	*ζ*-Bromohexylamine	1×10^{-3}
δ-Bromobutylamine	*ca.* 30		

The sequence obtained constitutes an excellent vindication of Ruzicka's theory of ring formation.[38] G. Salomon [39] discussed the accumulated data on the subject, and calculated the heat of activation and the action constant, *Z*, for the ring closures. It is shown that cyclisation can occur only if an activated molecule happens to be in the "ring position." The statistical equilibrium, ring position $\rightleftharpoons$ chain position, affects the value of *Z*. The length of the chain and, therefore, the deflexion of valency bonds, in forming the ring, influences the cyclisation velocity. Three- and four-membered rings demand a higher heat of activation than five- or six-membered rings, but a seven-membered ring also means a high activation energy, possibly owing to the interference of the chain-length factor. The ring position of the solute molecule appears to predominate when the solvent differs strongly from the solute from a physical point of view. For example, with ε-chloroamylamine and β-bromoethylamine, *Z* in water may be as much as 10^5—10^6 times greater than it is in organic solvents.

H. Freundlich and G. Salomon,[40] by studying the kinetics of the unimolecular cyclisation $CHPhCl{\cdot}CH_2{\cdot}NH_2 \longrightarrow$  $\underbrace{CHPh{-}CH_2}_{NH,HCl}$, find that the presence of a phenyl group, attached to the carbon atom carrying the reacting chlorine atom, greatly increases the speed of halogen elimination and weakens the resulting C–N ring bond. Similar work has been carried out by L. Ruzicka, G. Salomon, and K. E. Meyer,[41] who note that some of the higher members of the cyclic imine series have the musk odour already known to be possessed by certain *iso*cyclic analogues.

A. Müller and P. Bleier [42] prepared *cyclo*heptamethyleneimine in approximately 1% yield by reducing *cyclo*heptanone *iso*oxime or from αη-dibromoheptane, *p*-toluenesulphonamide, and alkali. The technique of the formation of cyclic imines has been greatly improved by Ruzicka and his co-workers. Thus,[43] *cyclo*octanone *iso*oxime (I), treated first with potassium sulphide and then with phosphorus pentasulphide, gives the corresponding thio*iso*oxime (II).

[38] L. Ruzicka, W. Brugger, M. Pfeiffer, H. Schinz, and M. Stoll, *Helv. Chim. Acta*, 1926, **9**, 499; *A.*, 1926, 727.

[39] *Helv. Chim. Acta*, 1933, **16**, 1361; *A.*, 1934, 34.

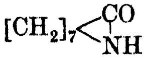
[40] *Z. physikal. Chem.*, 1933, **166**, 161; *A.*, 1933, 1125.

[41] *Helv. Chim. Acta*, 1934, **17**, 882; *A.*, 902.

[42] *Monatsh.*, 1930, **56**, 391; *A.*, 1931, 75.

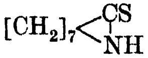
[43] L. Ruzicka, M. W. Goldberg, M. Hürbin, and H. A. Boekenoogen, *Helv. Chim. Acta*, 1933, **16**, 1323; *A.*, 1934, 82.

Reduction of (I) with sodium and ethyl alcohol, or of (II) electrolytically, gives *cyclo*octamethyleneimine (III). *cyclo*Pentadecamethyleneimine and *cyclo*hexadecamethyleneimine were obtained by similar processes; starting from *cyclo*triacontane-1 : 16-dione dioxime, there was obtained *cyclo*dipentadecamethylenedi-imine, which is either (IV) or (V).



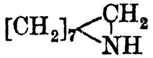
$[CH_2]_7<\begin{matrix}CO\\NH\end{matrix}$

(I.)



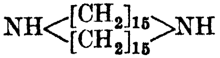
$[CH_2]_7<\begin{matrix}CS\\NH\end{matrix}$

(II.)



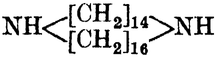
$[CH_2]_7<\begin{matrix}CH_2\\NH\end{matrix}$

(III.)



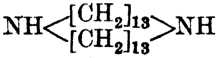
$NH<\begin{matrix}[CH_2]_{15}\\[CH_2]_{15}\end{matrix}>NH$

(IV.)



$NH<\begin{matrix}[CH_2]_{14}\\[CH_2]_{16}\end{matrix}>NH$

(V.)



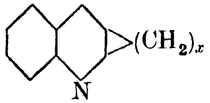
$NH<\begin{matrix}[CH_2]_{13}\\[CH_2]_{13}\end{matrix}>NH$

(VI.)

Similarly, A. Müller, E. Rölz, and M. Wiener [44] report the synthesis of *cyclo*ditridecamethyleneimine (VI).

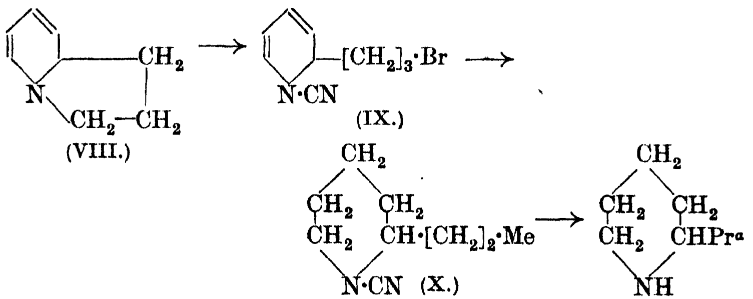
A novel application of the Friedländer quinoline synthesis is that in which L. Ruzicka, M. W. Goldberg, and M. Hürbin [45] condensed cyclic ketones with *o*-aminobenzaldehyde, and so obtained (VII), in which *x* is either 6 or 13.

(VII.)



When the vapour of hexamethyleneimine is passed over heated platinised asbestos, α-picoline is formed.[46]

Miscellaneous.—An interesting conversion of indolizidine into *dl*-coniine has been effected by E. Ochiai and K. Tsuda.[47] Indolizidine (VIII) reacts with cyanogen bromide to give (IX), which is reduced by means of palladium and hydrogen to the halogen-free compound (X). The latter affords *dl*-coniine when treated with hydrochloric acid :



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[44] *Ber.*, 1934, **67**, [*B*], 295; *A.*, 419.

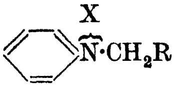
[45] *Helv. Chim. Acta*, 1933, **16**, 1335; *A.*, 1934, 86.

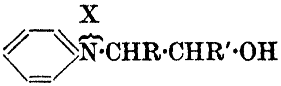
[46] M. Ehrenstein and I. Margraff, *Ber.*, 1934, **67**, [*B*], 486; *A.*, 534.

[47] *Ibid.*, p. 1011; *A.*, 901.

F. Kröhnke and K. Fasold[48] have found that a methyl or a methylene group attached to the nitrogen atom in pyridinium salts has marked reactivity. Thus, in general, a compound of the type (XI) reacts with an aldehyde, R′·CHO, to give a hydroxy-base (XII):

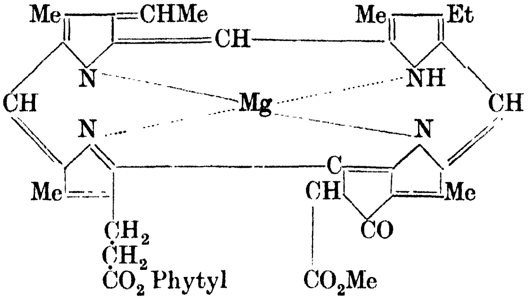
(XI.)



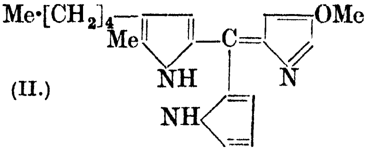


(XII.)

Natural and Other Colouring Matters.—H. Fischer and his co-workers have continued their valuable investigations on chlorophyll. The most recent formula (I) for chlorophyll-*a* is due to H. Fischer and J. Hasenkamp.[49] An account of his work was given by Fischer to the Chemical Society in the form of the Fourth Pedler Lecture.[50]



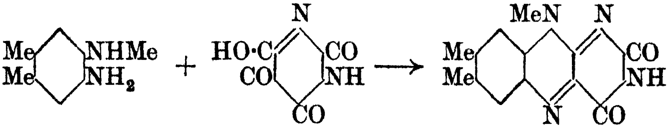
(I.)



(II.)

Prodigiosine, a red pigment isolated from *Bacillus prodigiosus*, has been shown by F. Wrede and A. Rothhaas[51] to have structure (II).

Lumi-lactoflavin, the colouring matter of lactoflavin (vitamin-*B*; vitamin-*G*), has been synthesised[52] by the condensation of alloxan with *N*-methyl-4 : 5-diamino-*o*-xylene :



(III.)

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[48] *Ber.*, 1934, **67**, [*B*], 656; *A.*, 663.

[49] *Annalen*, 1934, **513**, 107; *A.*, 1370.

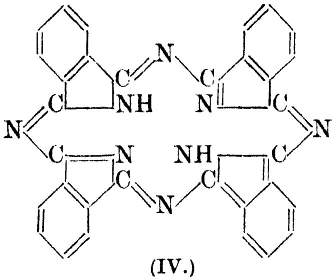
[50] *J.*, 1934, 245.

[51] *Z. physiol. Chem.*, 1934, **226**, 95; *A.*, 1232.

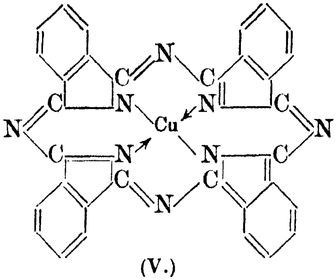
[52] R. Kuhn, R. Reinemund, and F. Weygand, *Ber.*, 1934, **67**, [*B*], 1460; *A.*, 1114.

The synthetic product (III) was in all respects identical with that obtained from milk.

Phthalocyanine is the name given [53] to a deep blue colouring matter to which the structure (IV) is assigned. It was formed as an impurity in phthalimide during the manufacture, in iron vessels, of the latter substance. The copper derivative (V) is very stable, as are the analogously constituted copper derivatives of phytochlorin and phytorhodin; it is unaffected by molten potassium hydroxide or by boiling hydrochloric acid. It can be recovered unchanged from its solution in concentrated sulphuric acid by addition of water, and can be sublimed at low pressures in an inert atmosphere.



(IV.)

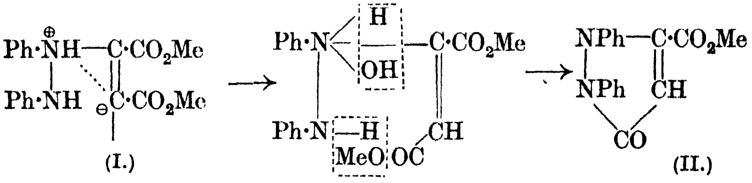


(V.)

Diene Syntheses of Heterocyclic Compounds.

(Continued from *Annual Reports*, 1933, **30**, 226.)

A further example of the fertile processes associated with this title is described by O. Diels and J. Reese.[54] Hydrazobenzene and methyl acetylenedicarboxylate combine readily in warm methyl-alcoholic solution to give a product which is regarded as having the structure (I), since (*a*) when warmed with acetic or mineral acid, it gives methyl 1 : 2-diphenyl-5-pyrazolone-3-carboxylate (II), presumably as the result of intermediate water addition; (*b*) when boiled



(I.) (II.)

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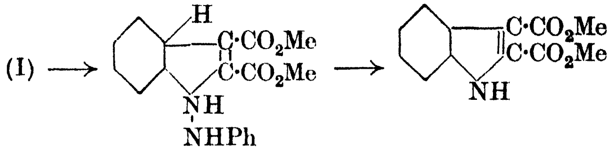
[53] R. P. Linstead, *J.*, 1934, 1016; G. T. Byrne, R. P. Linstead, and A. R. Lowe, *ibid.*, p. 1017; R. P. Linstead and A. R. Lowe, *ibid.*, p. 1022; C. E. Dent and R. P. Linstead, *ibid.*, p. 1027; R. P. Linstead and A. R. Lowe, *ibid.*, p. 1031; C. E. Dent, R. P. Linstead, and A. R. Lowe, *ibid.*, p. 1033; *A.*, 1114.

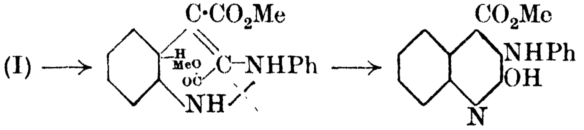
[54] *Annalen*, 1934, **511**, 168; *A.*, 903.

in xylene solution, it loses aniline to give methyl indole-2 : 3-dicarboxylate (III) :



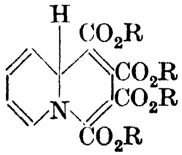
(III.)

and (*c*) when heated to its melting point or to the boiling point of its pyridine or dimethylaniline solution, it gives some of the indole ester, but is mainly converted into methyl 3-anilino-2-hydroxyquinoline-4-carboxylate (IV) :

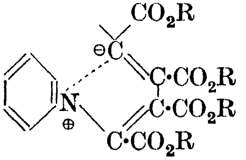


(IV.)

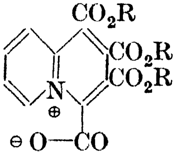
It was shown by Diels and Alder [55] that pyridine and methyl acetylenedicarboxylate in ethereal solution gave three coloured compounds (V, VI, and VII) :



(V.)



(VI.)



(VII.)

In acetic acid solution, mellitic esters are formed. It is now found [56] that in methyl-alcoholic solution at 0° there is produced a colourless compound (XV). The mechanism suggested for the reaction is as follows : Two molecules of methyl acetylenedicarboxylate combine, as in ethereal solution, to give (VIII), which adds on two molecules of methyl alcohol to form (IX). The latter may decompose into two molecules of methyl methoxyfumarate (X), which was actually found in the mother-liquors. Alternatively, (VIII) may combine with one molecule of methyl alcohol to give (XI), which combines with pyridine, forming (XII). Rearrangement of (XII) to (XIII), followed (*a*) by loss of methyl methoxyacetate gives methyl indolizinetricarboxylate (XIV), or (*b*) by loss of methyl formate, gives the colourless compound (XV).

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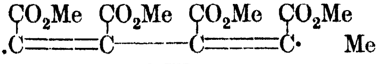
[55] *Annalen*, 1932, **498**, 16; 1933, **505**, 103; 1934, **510**, 87; *A.*, 1932, 1144; 1933, 1058; 1934, 782.

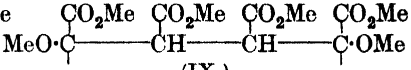
[56] O. Diels and R. Meyer, *ibid.*, 1934, **513**, 129; *A.*, 1367.

Either course is possible. Pyridine and the acetylene ester in methyl-alcoholic solution, *without cooling*, give indolizinetricarboxylic ester (XIV), but, *with good cooling*, the colourless compound (XV) is formed.



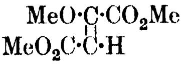
$$\overset{CO_2Me}{.C}=\overset{CO_2Me}{C}-\overset{CO_2Me}{C}=\overset{CO_2Me}{C}\cdot$$

(VIII.)



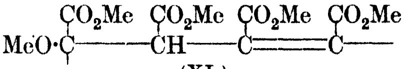
$$MeO\cdot\overset{CO_2Me}{\underset{|}{C}}-\overset{CO_2Me}{CH}-\overset{CO_2Me}{CH}-\overset{CO_2Me}{\underset{|}{C}}\cdot OMe$$

(IX.)



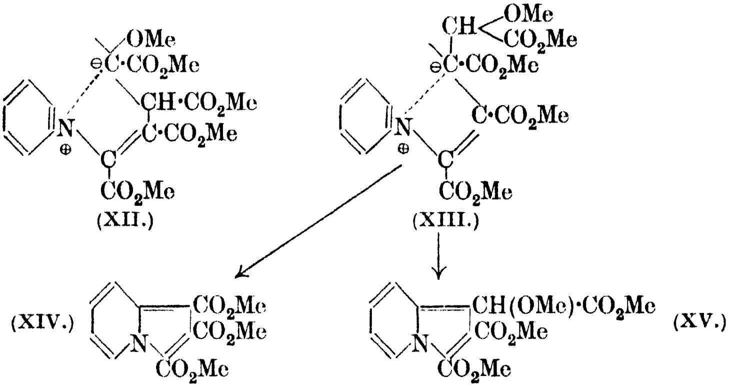
$$\begin{array}{c}MeO\cdot C\cdot CO_2Me\\ \| \\ MeO_2C\cdot C\cdot H\end{array}$$

(X.)



$$MeO\cdot\overset{CO_2Me}{\underset{|}{C}}-\overset{CO_2Me}{CH}-\overset{CO_2Me}{C}=\overset{CO_2Me}{C}-$$

(XI.)



(XII.) (XIII.) (XIV.) (XV.)

Alkaloids.

A useful account of recent synthetical work in the alkaloid series was given by E. Späth.[57]

Indole Group.—A convenient synthesis of *dl*-eserethole has been described by F. E. King, M. Liguori, and R. Robinson:[58] γ-phthalimido-α-methylbutyric acid was converted into the acid chloride, the amide and the nitrile, which, when reduced by Stephens's method, gave γ-phthalimido-α-methylbutaldehyde,

$$C_6H_4{:}(CO)_2{:}N\cdot CH_2\cdot CH_2\cdot CHMe\cdot CHO.$$

This compound and *p*-ethoxyphenylhydrazine were condensed to give 5-ethoxy-3-methyl-3-(β-phthalimidoethyl)indolenine (I), which was converted into its methosulphate. This was treated successively with hydrazine in ethyl alcohol and with hydrochloric acid, and gave *dl*-noreserethole (II), from which, by methylation, *dl*-eserethole was obtained.

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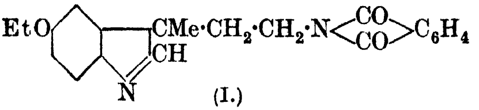
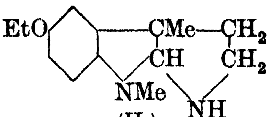
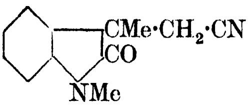
[57] *Bull. Soc. chim.*, 1933, [iv], **53**, 1358.

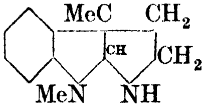
[58] *J.*, 1933, 1475; *A.*, 1934, 89; *J.*, 1934, 1416; *A.*, 1236; compare R. Robinson and H. Suginome, *J.*, 1932, 304; *A.*, 1932, 287.

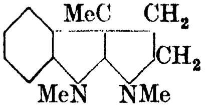

(I.)


(II.)

P. L. Julian, J. Pikl, and D. Boggess[59] have effected the following synthesis of deoxyeseroline: 1 : 3-dimethyloxindole, with chloroacetonitrile and sodium ethoxide, gave the nitrile (III), which, when reduced, gave deoxynoreseroline (IV), from which deoxyeseroline (V) was obtained by the action of methyl iodide.

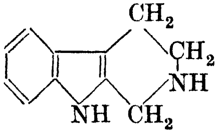

(III.)

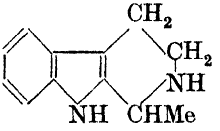

(IV.)


(V.)

Simple syntheses of naturally occurring compounds or of compounds related to them are always attractive, and particularly so when the conditions employed resemble those available in living matter. E. Späth and E. Lederer[60] obtained tetrahydro-β-carboline (VI) by heating 3-β-aminoethylindole with formaldehyde solution for one minute in presence of dilute sulphuric acid and extracting the product in ether and boiling it with dilute acid. S. Akabori and K. Saito[61] effected the analogous reaction with acetaldehyde in presence of dilute sulphuric acid at 110° for twenty minutes, and recently G. Hahn and H. Ludewig[62] have shown that the same condensation (giving tetrahydroharman, VII) proceeds almost quantitatively at room temperature in one day in a solution buffered at p_H 5, 6, or 7. These authors have similarly prepared 3-benzyltetrahydroharman from phenylacetaldehyde.

(VI.)





(VII.)

Yohimbine.—A valuable critical survey of existing and new experimental data is given by G. Barger and C. Scholz.[63] It was known[64] that the action of selenium on yohimbine produced yobyrine, dihydroyobyrine, and ketoyobyrine. Barger and Scholz conclude that yobyrine and tetrahydroyobyrine (Wibaut's dihydroyobyrine) are respectively (I) and (II). The presence of the system ABC is shown by the formation of harman as a degradation product of yohimbine.[65] Oxidation of tetrahydroyobyrine with nitric acid is found to give berberonic acid (III). This gives the clue to ring D, and so explains the formation of some *iso*quinoline when yohimbine is distilled with zinc dust.[66] The observation of Mendlik and Wibaut [64] that potassium hydroxide fusion of ketoyobyrine gave 2 : 3-dimethylbenzoic acid is connected with the opening of ring D; the two methyl groups correspond to C_{14} and C_{21}, and the carbonyl group is at C_{16} or C_{19} and is probably (as Mendlik and Wibaut assumed) in the position occupied by the carboxylic acid group in yohimboaic acid. Ketoyobyrine is formed by a ring closure, most probably at N_1, since Mendlik and Wibaut obtained no ketoyobyrine from diacetylyohimbine. Potash fusion of ketoyobyrine almost certainly separates the atoms C_{14} to C_{22}* as dimethylbenzoic acid, and N_1–C_2–C_{13} give rise to the Mendlik and Wibaut product $C_{11}H_{10}O_2N_2$, which is probably a norharman derivative. By conducting the "potash fusion" of ketoyobyrine in amyl alcohol, Barger and Scholz also obtained hemimellitic acid and norharman, which identifies the ketoyobyrine skeleton. In the above degradations, C_{14} remains attached to ring E. It is separated from E and left attached to C when yohimbine or yohimboaic acid is fused with potassium hydroxide or treated with superheated steam, the *m*-toluic acid formed presumably containing the original carboxyl group, but not C_{14}. The identity of the skeletons of yohimbine and yobyrine is not proved, but little doubt can be entertained that the ring structure of yohimbine persists in the primary dehydrogenation product, tetrahydroyobyrine. This compound has been obtained by two new processes: potash fusion of yohimboaic acid or treatment of the latter with superheated steam. In absence of a positive

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[59] *J. Amer. Chem. Soc.*, 1934, **56**, 1797; *A.*, 1116.

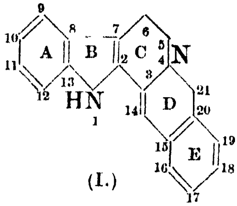
[60] *Ber.*, 1930, **63**, [*B*], 2102; *A.*, 1930, 1448; *Ann. Reports*, 1930, **27**, 184.

[61] *Ber.*, 1930, **63**, [*B*], 2245; *A.*, 1930, 1445.

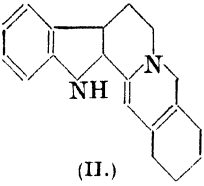
[62] *Ber.*, 1934, **67**, [*B*], 2031.

[63] *Helv. Chim. Acta*, 1933, **16**, 1343; *A.*, 1934, 89.

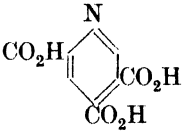
[64] F. Mendlik and J. P. Wibaut, *Rec. trav. chim.*, 1931, **50**, 91; *A.*, 1931, 369; *Ann. Reports*, 1932, **29**, 207.



(I.)



(II.)



(III.)

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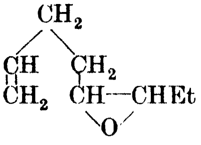
[65] G. Barger and C. Scholz, *J.*, 1933, 614; *A.*, 1933, 840.

[66] E. Winterstein and M. Walter, *Helv. Chim. Acta*, 1927, **10**, 577; *A.*, 1927, 1208.

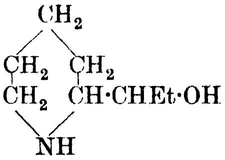
* The carbon atom of the carboxyl group in yohimboaic acid is numbered 22, and that of the methyl group 23.

test for NMe, the tertiary nitrogen atom must belong to the two rings C and D. Oxidation of yohimbine gives only succinic acid, indicating the reduced nature of C, D, and E. The authors picture yohimbine as having tryptophan and phenylalanine as its phytochemical precursors. G. Hahn, E. Kappes, and H. Ludewig[67] dehydrogenated yohimbine by means of lead tetra-acetate, and arrived at a yohimbine skeleton essentially the same as that already suggested by Barger and Scholz. Hahn and his co-workers conclude that the carboxyl group in yohimboaic acid is attached to C_{16}, but Barger[68] regards this conclusion as invalid. Hahn[69] thinks that the gentle dehydrogenation of yohimbine with lead tetra-acetate and the splitting of the resulting tetrahydroyobyrine with amyl-alcoholic potassium hydroxide (giving harman and *m*-toluic acid) definitely permit of the assignment of the carboxyl group to C_{16}.

Piperidine Derivatives.—Dehydration of conhydrine, followed by reduction of the product, produces dihydroconiceine, which is identical with *l*-coniine. Exhaustive methylation of conhydrine gives the oxide (I), whence it follows that the alkaloid is α-hydroxyconiine (II).[70]



(I.)



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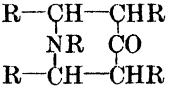
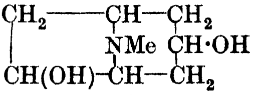


(III.)



(IV.)

A number of "open" tropines (III) have been prepared by C. Mannich[71] by condensing acetaldehyde with primary amines and either methyl acetonedicarboxylate or potassium methyl potassioacetonedicarboxylate. Among the compounds obtained are "open" ecgonine, ψ-ecgonine, cocaine, and psicaine. The salts of both *d*- and *l*- "open" cocaine have marked anæsthetic action. The *l*-series has the more pronounced action, and is also the more poisonous. "Open" cocaine has far less anæsthetic action than cocaine. Similarly, the tropyl ester of "open" ψ-tropine (stereochemically related, not to atropine, but to the tropyl ester of ψ-tropine) has a mydriatic action about one-hundredth of that of atropine.

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[67] *Ber.*, 1934, **67**, [*B*], 686; *A.*, 667.

[68] *Ibid.*, p. 1124; *A.*, 907.

[69] *Ibid.*, p. 1211; *A.*, 907.

[70] E. Späth and E. Adler, *Monatsh.*, 1933, **63**, 127; *A.*, 1934, 87.

[71] *Arch. Pharm.*, 1934, **272**, 323; *A.*, 667.

A new dihydroxytropan (IV) has been isolated from *Coca* leaves.[72]

Lupin Alkaloids.—K. Winterfeld and A. Kneuer [73] stated that reduction of lupanine with phosphorus and hydriodic acid gave β-lupinane. G. R. Clemo, (Miss) G. C. Leitch, and R. Raper[74] failed to obtain this result, which was, however, confirmed by K. Winterfeld, A. Kneuer, and F. W. Holschneider.[75] Clemo and Raper [76] now find that specially purified racemic lupanine gives no β-lupinane, and that this substance arises from lupinine, present as an impurity. On the other hand, Winterfeld and Holschneider [77] confirm their own results, and attribute the failure recorded by Clemo and Raper to the use of insufficient material.

Dehydrosparteine, as formerly obtained by the action of mercuric acetate on sparteine, is now shown [78] to contain two (α- and β-) didehydrosparteines. The hydrogenation of pure dehydrosparteine gives sparteine; that of α-didehydrosparteine gives α-*iso*sparteine, a crystalline solid; that of β-didehydrosparteine gives β-*iso*sparteine, a liquid, which is probably identical with *d*-sparteine.[79] K. Winterfeld and C. Rauch regard R. H. Ing's sparteine formula [80] as more satisfactory than that of Clemo and Raper.[81]

Related to this subject is a publication by A. Orékhov and S. Norkina.[82] Aphyllidine, $C_{15}H_{22}ON_2$, had already [83] been isolated from the high-boiling fraction of the *Anabasis aphylla* alkaloid mixture. It is now shown that aphyllidine, on electrolytic reduction, gives a base, $C_{15}H_{26}N_2$, identical (i) with pachycarpine, from *Sophora pachycarpa* [84] and *Thermopsis lanceolata*,[85] and (ii) with *d*-sparteine. On the other hand, electrolytic reduction of sophocarpine, from *S. pachycarpa*, and of sophoridine, from *S. Alopecuroides*, gives two new bases, $C_{15}H_{26}N_2$, entirely distinct from pachycarpine.

Quinoline Alkaloids.—Considerable disagreement has existed as to the constitutions of peganine and vasicine. Vasicine was isolated from the leaves of *Adnatoda vasica*, Nees, by J. N. Sen and T. P.

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[72] O. Wolfes and O. Hromatka, *Mercks Jahresber.*, 1934, **47**, 45; *A.*, 1935, 98.

[73] *Ber.*, 1931, **64**, [*B*], 150; *A.*, 1931, 371.

[74] *Ibid.*, p. 1520; *A.*, 1931, 970.

[75] *Ibid.*, p. 2415; *A.*, 1931, 1433.

[76] *Ber.*, 1934, **67**, [*B*], 463; *A.*, 538.

[77] *Ibid.*, p. 778; *A.*, 787.

[78] K. Winterfeld and C. Rauch, *Arch. Pharm.*, 1934, **272**, 273; *A.*, 668.

[79] G. R. Clemo, R. Raper, and C. R. S. Tenniswood, *J.*, 1931, 429; *A.*, 1931, 498.

[80] *J.*, 1933, 504; *A.*, 1933, 727.

[81] *Ibid.*, p. 644; *A.*, 1933, 841.

[82] *Ber.*, 1934, **67**, [*B*], 1845; *A.*, 1935, 97.

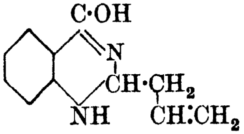
[83] A. Orékhov and G. Menschikov, *Ber.*, 1932, **65**, [*B*], 234; *A.*, 1932, 405.

[84] A. Orékhov, M. Rabinovitsch, and R. Konovalova, *Ber.*, 1933, **66**, [*B*], 621; *A.*, 1933, 617.

[85] A. Orékhov, S. Norkina, and H. Gurevitsch, *ibid.*, p. 625; *A.*, 1933, 617.

Ghose,[86] and further investigation [87] led to the constitution (I). Potash fusion of vasicine gave anthranilic acid, and permanganate oxidation gave 4-quinazolone. Vasicine, when heated with alkali, gave *iso*vasicine, in which the unsaturated side chain was no longer active, and which was therefore regarded as (II). E. Späth and E. Nikawitz [88] obtained peganine from the technical residues of the preparation of the alkaloids of *Peganum harmala*. By oxidation, followed by treatment of the product with diazomethane, they obtained methyl 4-keto-3 : 4-dihydroquinazolyl-3-acetate (III), which was converted by alkali into anthranilic acid and glycine. The acid corresponding to (I), when decarboxylated, gave 4-keto-3-methyl-3 : 4-dihydroquinazolone. The alkaloid was reduced by sodium and amyl alcohol to deoxytetrahydropeganine, which contains an imino-group, and by tin and hydrochloric acid to deoxyhexahydropeganine. Peganine was therefore assigned structure (IV), and the possibility of its identity with vasicine was left open.

(I.)



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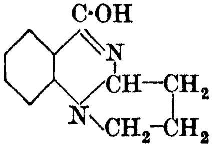
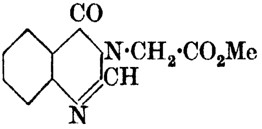


(III.)



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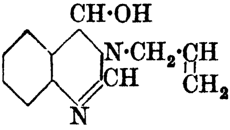

E. Späth and F. Kuffner,[89] by comparing a number of derivatives of peganine and vasicine, concluded that the two alkaloids were identical, but K. S. Narang and J. N. Rây [90] said that this was not so, since vasicine dissolved in alkali and was precipitated therefrom by acetic acid, and since acetic anhydride converted vasicine into a compound which contained one molecule of water less than a normal acetyl derivative. On the other hand, E. Späth and F. Kuffner [91] found that Merck's vasicine and peganine gave the same melting point and mixed melting point, the same hydrochloride, and the same chlorodeoxy-derivative. They concluded that the Indian workers were dealing with a different alkaloid, and produced further proof of the constitution of peganine by synthesising the ester (III). Isatoic anhydride (V) was treated with glycine ester hydrochloride and sodium methoxide; the resulting ester (VI), when heated with formic acid, gave (III):

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[86] *J. Indian Chem. Soc.*, 1925, **1**, 315; *A.*, 1925, i, 958.

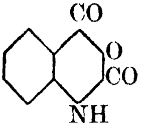
[87] T. P. Ghose, S. Krishna, K. S. Narang, and J. N. Rây, *J.*, 1932, 2740; *A.*, 1933, 77.

[88] *Ber.*, 1934, **67**, [*B*], 45; *A.*, 310.

[89] *Ibid.*, p. 868; *A.*, 787.

[90] *Current Science*, 1934, **2**, 388; *A.*, 905.

[91] *Ber.*, 1934, **67**, [*B*], 1494; *A.*, 1235.



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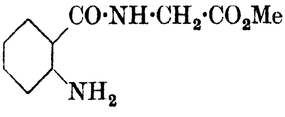

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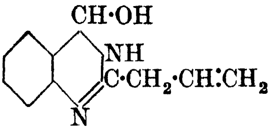
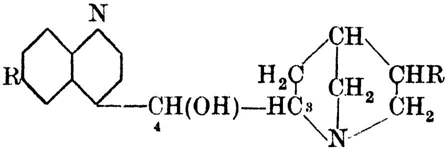


(VII.)

The authors added that peganine might possibly contain a ring structure between the propenyl side chain and the 4-hydroxyl group. K. S. Narang and J. N. Rây [92] then advanced formula (VII) for vasicine, and (Miss) T. M. Reynolds and R. Robinson [93] obtained a compound, evidently having structure (IV), by treating with alkali the quaternary salt formed from quinazoline and allyl iodide. The compound formed was not identical with vasicine.

Cinchona Alkaloids.—H. Emde [94] regarded all stereoisomerism in the cinchona alkaloids (VIII) as being due to the spatial arrangement of the carbinol group C_4, and not involving also C_3, as suggested by H. King and A. D. Palmer [95] and by P. Rabe.[96] A former writer of these Reports [94] commented critically on this, and it is therefore interesting to find that P. Rabe, H. Haeuszler, and W. Hochstätter [97] show Emde's conclusions to be based on incorrect experimental observations. Hydrocinchonidine, when heated with 25% hydrochloric acid, gives, not, as Emde stated, hydrocinchotoxine, but the known epihydrocinchonidine; similarly, hydrocinchonine gives the known epihydrocinchonine.



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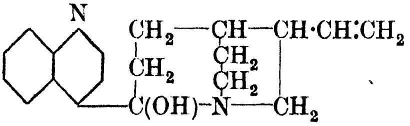

(IX.)

In the same memoir, Rabe shows that the epicinchonine described by J. Suszko and A. Tomanek [98] is in fact not a stereoisomeride but the structural isomeride (IX), and should be called *hetero* or *h*-cinchonine.

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[92] *Chem. and Ind.*, 1934, 698; *A.*, 1014.

[93] *Nature*, 1934, **134**, 142; *A.*, 1014.

[94] *Helv. Chim. Acta*, 1932, **15**, 557; *A.*, 1932, 759; *Ann. Reports*, 1932, **29**, 185.

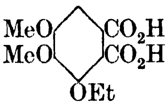
[95] *J.*, 1922, **121**, 2577.

[96] *Annalen*, 1932, **492**, 242; *A.*, 1932, 289.

[97] *Ibid.*, 1934, **514**, 61; *A.*, 1935, 99.

The antimalarial drugs "plasmoquin" (a compound of 1 : 1′-methylene-2 : 2′-dinaphthyl-3 : 3′-dicarboxylic acid and 8-δ-diethylamino-α-methylbutylamino-6-methoxyquinoline) and "atebrin" (6-chloro-9-δ-diethylamino-α-methylbutylamino-2-methoxyacridine) have been investigated.[99]

iso*Quinoline Alkaloids.*—From the fact that pellotine *O*-ethyl ether, obtained from the alkaloid and diazoethane, was oxidised by permanganate to 4 : 5-dimethoxy-3-ethoxyphthalic acid (I), E. Späth [1] concluded that pellotine is (II), and anhalonidine, since it (i) is obtained by ring closure from β-3-acetoxy-4 : 5-dimethoxyphenylethylamine, (ii) is a secondary base, and (iii) gives the same quaternary compound as pellotine when it is methylated only on the nitrogen atom, must be (III). The proof of the constitution of the phthalic acid is of interest: 1 : 2 : 3 : 5 : 6 : 7-hexahydroxyanthraquinone with diazomethane gave a tetramethyl ether which must be (IV), since it does not give trimethoxyphthalic acid when it is oxidised. Ethylation of (IV), followed by oxidation of the product, gave an acid identical with (I), the constitution of which is thus proved. Later, E. Späth and F. Boschan [2] reduced pellotine *O*-ethyl ether methochloride, and treated the methiodide of the product with alkali; in addition to trimethylamine, 4 : 5-dimethoxy-3-ethoxy-2-ethylstyrene was then evidently formed, since oxidation gave 4 : 5-dimethoxy-3-ethoxy-2-ethylbenzoic acid. The con-



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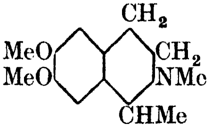

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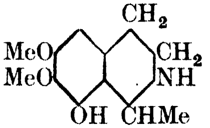
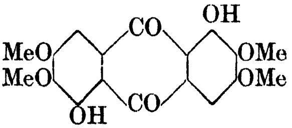
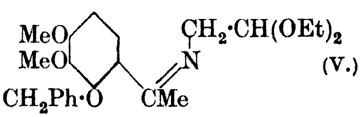


(III.)

(IV.)





(V.)

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[98] *Rec. trav. chim.*, 1933, **52**, 18; *A.*, 1933, 288.

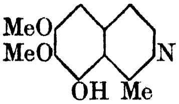
[99] I. L. Knunjantz, K. S. Toptschiev, and G. V. Tschelintzev, *Bull. Acad. Sci. U.R.S.S.*, 1934, **8**, No. 1, 153; *B.*, 650; I. L. Knunjantz, G. V. Tschelintzev, Z. V. Benevolenskaja, E. D. Ostrova, and A. I. Kursanova, *ibid.*, p. 165; *B.*, 650.

[1] *Ber.*, 1932, **65**, [*B*], 1778; *A.*, 1933, 77.

[2] *Monatsh.*, 1933, **63**, 141; *A.*, 1934, 87.

stitution of this acid was proved by a method involving synthesis. Finally, E. Späth and F. Becke[3] synthesised pellotine from 2-hydroxy-3 : 4-dimethoxyacetophenone. The benzyl ether of this substance condensed with aminoacetal to give (V), which, in presence of 73% sulphuric acid, gave 8-hydroxy-6 : 7-dimethoxy-1-methyl*iso*quinoline (VI). Reduction of the methiodide of this base produced pellotine, which is therefore (II).

In 1921, E. Späth[4] proposed three alternative structures for anhalamine, one of which was ruled out in 1922.[5] Decision between the two remaining formulæ (VII) and (VIII) has now been made[6] as follows: anhalamine with ethyl iodide in presence of sodium ethoxide gives *N*-ethylanhalamine *O*-ethyl ether ethiodide. The corresponding quaternary hydroxide is oxidised by potassium permanganate to 4 : 5-dimethoxy-3-ethoxyphthalic acid (I), so that anhalamine is (VIII) and not (VII). It follows that these phenol bases occurring in the related cacti *Anhalonium Williamsi* and *A. Lewinii*, Hennings, have the same disposition of hydroxyl and methoxyl groups.



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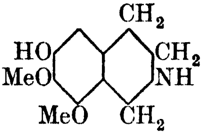
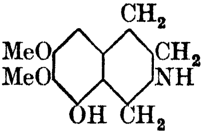
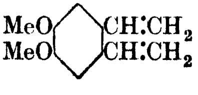


(VII.)

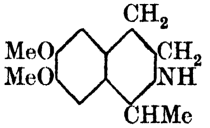


(VIII.)

From *Salsola Richteri* (Chenopodiaceae), A. Orékhov and N. Proskurnina[7] isolated an alkaloid salsoline, which was evidently closely related to carnegine, and less closely to anhalonidine, anhalonine, pellotine, and lophophorine. Hofmann degradation of *O*-methylsalsoline led to trimethylamine and an acid, $C_{12}H_{10}O_2$, oxidation of which gave *m*-hemipinic acid. The former acid was therefore (IX), and *O*-methylsalsoline was (X). Nitrogen methylation, effected by means of formaldehyde and formic acid, converted *O*-methylsalsoline into carnegine, known to be (XI). Recently,



(IX.)



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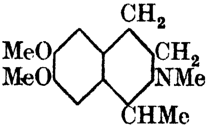

(XI.)

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[3] *Ber.*, 1934, **67**, [*B*], 266; *A.*, 423.

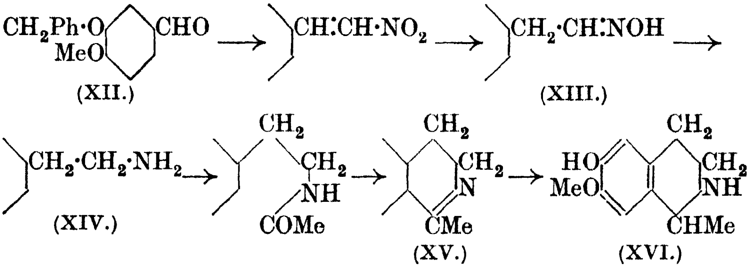
[4] *Monatsh.*, 1921, **42**, 97; *A.*, 1922, i, 163.

[5] *Ibid.*, 1922, **43**, 93; *A.*, 1922, i, 852.

[6] E. Späth and F. Becke, *Ber.*, 1934, **67**, [*B*], 2100.

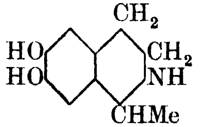
[7] *Ber.*, 1933, **66**, [*B*], 841; *A.*, 1933, 727.

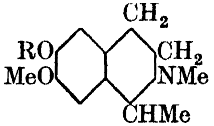
salsoline was synthesised.[8] *iso*Vanillin benzyl ether (XII) was condensed with nitromethane. Reduction of the product gave, successively, (XIII) and (XIV), the acetyl derivative of which was readily cyclised by the phosphoric oxide–toluene method to give (XV). Reduction of this compound with tin and hydrochloric acid produced salsoline, which is therefore (XVI).



Interesting syntheses of compounds allied to salsoline have been recorded by C. Schöpf and H. Bayerle.[9] It is found that when β-3 : 4-dihydroxyphenylethylamine hydrobromide is kept in a $M/25$-aqueous solution with $M/12{\cdot}5$-acetaldehyde for three days, the p_H of the solution remains approximately 5·0, and an 83% yield of norsalsoline (XVII) is formed.

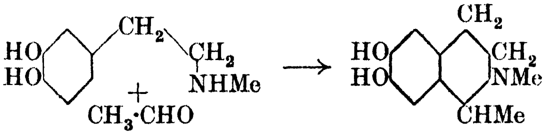
(XVII.)





(XVIII.)

The supposition that carnegine (XVIII; R = Me) and salsoline originate naturally in this manner in presence of an enzyme[10] explains why these two alkaloids appear as racemates.[11] Schöpf and Bayerle have also shown that the condensation proceeds at p_H 4 at 25° in three days.



The following synthesis of *dl*-homolaudanosine has been described:[12] Diveratrylideneacetone (XIX) was reduced to di-(β-3 : 4-dimethoxyphenyl)ethyl ketone (XX), the oxime of which, in toluene solution, in presence of phosphoric oxide, underwent Beckmann rearrangement and then ring closure to (XXI). The methochloride of this, when reduced catalytically, gave *dl*-homolaudanosine, which with hydriodic acid gave *dl*-homolaudanosoline (XXII).

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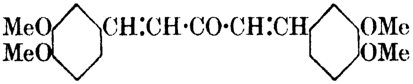
[8] E. Späth, A. Orékhov, and F. Kuffner, *Ber.*, 1934, **67**, [*B*], 1214; *A.*, 907.

[9] *Annalen*, 1934, **513**, 190; *A.*, 1373.

[10] Compare C. Schöpf, *Annalen*, 1932, **497**, 1; *A.*, 1932, 1046.

[11] G. Barger, IX Congreso Internacional de Química Pura y Aplicada, Conferencias de Introduccion, Madrid, 1934, 177.

[12] S. Sugasawa and H. Yoshikawa, *J.*, 1933, 1583; *A.*, 1934, 196.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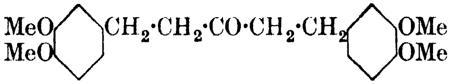
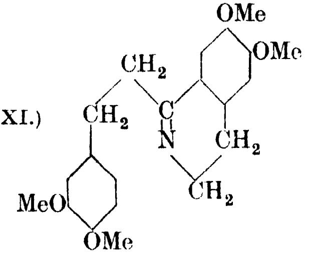
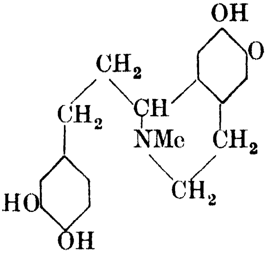
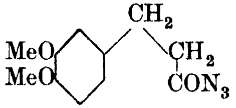
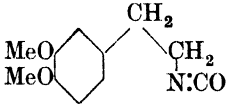

(XX.)

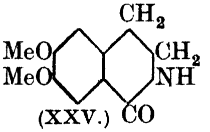
(XXI.)



(XXII.)

L. M. Mohunta and J. N. Rây [13] have effected the synthesis of corydaldine. The azide (XXIII) in boiling toluene solution was converted into the carbimide (XXIV), which gave corydaldine (XXV) when treated with phosphoryl chloride :


(XXIII.)


(XXIV.)


(XXV.)

An interesting communication has been published on the stereoisomerides of narcotine and hydrastine.[14] When *l*-α-narcotine is heated with methyl-alcoholic potassium hydroxide, racemisation (presumably at the phthalide carbon atom) occurs, and from the equilibrium mixture formed, *l*-β-narcotine has been isolated. Similarly, from natural *l*-hydrastine (regarded as *l*-β-hydrastine), *l*-α-hydrastine has been obtained.

Phenanthridine Alkaloid.—Tazettine, isolated by E. Späth and L. Kahovec,[15] from *Narcissus Tazetta*, L., may be identical (i) with sekisanine, which accompanies lycorine in *Lycoris radiata*,[16] and

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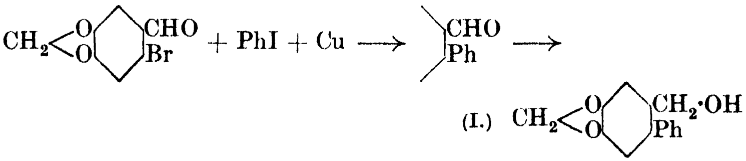
[13] *J.*, 1934, 1263; *A.*, 1111.

[14] (Miss) M. A. Marshall, F. L. Pyman, and R. Robinson, *ibid.*, p. 1315; *A.*, 1236.

[15] *Ber.*, 1934, **67**, [*B*], 1501; *A.*, 1237.

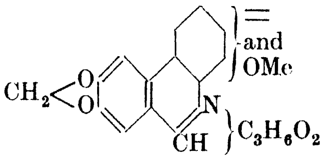
[16] K. Morishima, *Arch. exp. Path. Pharm.*, 1897, **40**, 221; *A.*, 1899, i, 92.

(ii) with "Base VIII" of H. Kondo, K. Tomimura, and S. Ishiwatari.[17] Tazettine is oxidised to hydrastic acid, and affords phenanthridine when distilled with zinc dust. Tazettine methiodide was converted into a methine base, which spontaneously lost methyl alcohol, and gave a methiodide, Hofmann degradation of which gave 6-phenylpiperonyl alcohol (I), identical with the end product of the following synthesis:

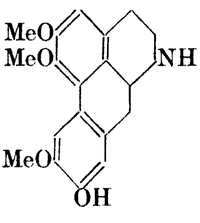


From these results the partial formula of tazettine (II) is deduced.

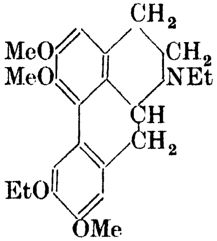
(II.)



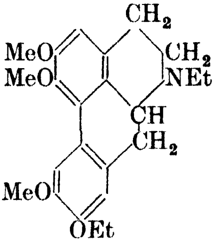
Aporphine Alkaloids.—The constitution (III) of laurotetanine from *Litsea citrata*, Bl., was established by G. Barger, J. Eisenbrand, L. Eisenbrand, and E. Schlittler,[18] and shortly afterwards by E. Späth and K. Tharrer.[19] The former workers synthesised two compounds (IV) and (V) by the following process: vanillin ethyl ether (for IV) or *iso*vanillin ethyl ether (for V), R·CHO, was converted into the azlactone, thence into the pyruvic acid, $R·CH_2·CO·CO_2H$, and the acetic acid, $R·CH_2·CO_2H$. Nitration of these two acids was followed by preparation of the homoveratroylamides, which were then converted into (IV) and (V). Hofmann degradation of (V) led to 3 : 5 : 6-trimethoxy-2-ethoxy-8-vinylphenanthrene,



(III.)



(IV.)



(V.)

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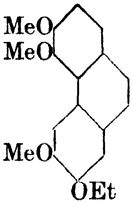
[17] *J. Pharm. Soc. Japan*, 1932, **52**, 51.

[18] *Ber.*, 1933, **66**, [*B*], 450; *A.*, 1933, 405.

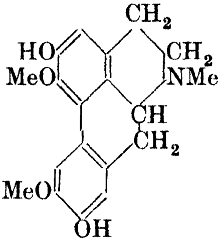
[19] *Ibid.*, p. 583; *A.*, 1933, 518.

identical with the product obtained by a similar process from *ON*-diethyl-laurotetanine; so the alkaloid must be (III). Späth and Tharrer converted laurotetanine into its ethyl ether, and then into the methiodide of the latter. Decomposition of the methohydroxide gave a methine base, and this, in turn, gave a methiodide. The base from the latter gave trimethoxyethoxyvinylphenanthrene, and oxidation of this substance, followed by decarboxylation, produced trimethoxyethoxyphenanthrene (VI), identical with the product of decarboxylating synthetic 3 : 5 : 6-trimethoxy-2-ethoxyphenanthrene-10-carboxylic acid; whence laurotetanine is (III).

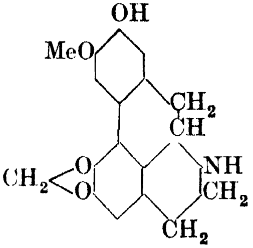
Similarly, E. Späth and K. Tharrer[20] have shown that boldine, from *Boldea fragrans*, Juss, is (VII).



(VI.)



(VII.)



(VIII.)

The alkaloid actinodaphnine was isolated by S. Krishna and T. P. Ghose[21] from *Actinodaphne Hookeri*, Meissn (Nat. order, *Lauraceae*). In conjunction with E. Schlittler[22] the same authors have elucidated its probable constitution. The data obtained are as follows: Actinodaphnine, which is oxidised to methylenedioxyhemimellitic acid, forms an *O*-methyl ether, converted by methyl iodide and sodium methoxide into a methiodide, which, with sodium hydroxide, affords a methine base. The last is methylated (methyl iodide and silver oxide) to a dimethoxymethylenedioxyvinylphenanthrene, from which the vinyl group is eliminated by oxidation, followed by decarboxylation. *m*-Hemipinic acid is obtained by the oxidation of actinodaphnine, the *O*-methyl ether of which, when treated first with methyl iodide and secondly with acetic anhydride, gives *N*-acetyl-*O*-methylactinodaphnine, together with dicentrine. The latter alkaloid is formed by the *N*-methylation of actinodaphnine. *N*-Methyl-*O*-ethylactinodaphnine is converted by sulphuric acid and phloroglucinol into a dihydroxy-compound, the dimethyl ether of which, when submitted to Hofmann degradation, gives the above trimethoxyethoxyvinylphenanthrene obtained from laurotetanine.

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[20] *Ber.*, 1933, **66**, [*B*], 904; *A.*, 1933, 840.

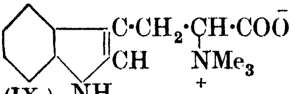
[21] *J. Indian Chem. Soc.*, 1932, **9**, 429; *A.*, 1933, 168.

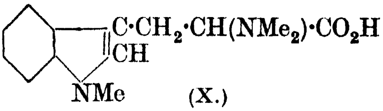
[22] *Helv. Chim. Acta*, 1934, **17**, 919; *A.*, 1236.

Strychnine.—M. Kotake and T. Mitsuwa [23] have proposed a new formula for strychnine, but R. Robinson [24] has shown that it fails to account for much of the chemistry of the alkaloid. Among recent papers on strychnine and its allies should be mentioned five by R. Robinson and his collaborators.[25] In the second of these papers is described the successful application of Hofmann degradation to metho-derivatives of dihydrostrychnidine-A.

Toad Poison.—H. Wieland, G. Hesse, and H. Mittasch [26] isolated bufotenine from the skin of toads (*Bufo vulgaris*). Analyses of the picrate and the methiodide suggested that bufotenine was $C_{14}H_{18}O_2N_2$. Degradation of bufotenine gave a base, bufotenidine, present in bufotenine extraction mother-liquors and identical with a base isolated by Mittasch from Chinese *Senso*. By analogy with hyaphorine (IX), bufotenine was regarded as (X), and bufotenidine as (XI). It has now been shown [27] that the former method of separation of bufotenine as flavianate or picrate is unsatisfactory, but pure bufotenine oxalate is readily obtainable, and is found to be $C_{12}H_{16}ON_2,H_2C_2O_4,H_2O$. The usual methods of attack on the constitution (Hofmann and Emde degradation, oxidation, etc.) gave no positive results. Bufotenine methiodide is identical with bufotenidine hydriodide. Bufotenine and methyl iodide, in presence of alcoholic thallium ethoxide, gave *O*-methylbufotenine metho-salts, also obtained by methylating bufotenidine with methyl sulphate and alkali. Bufotenine therefore contains (i) the indole skeleton, (ii) a hydroxyl group attached thereto, and (iii) a dimethyl-

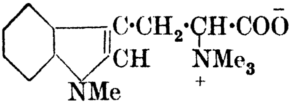
(IX.)





(X.)

(XI.)



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[23] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **24**, 119; *A.*, 908.

[24] *J.*, 1934, 1490; *A.*, 1374.

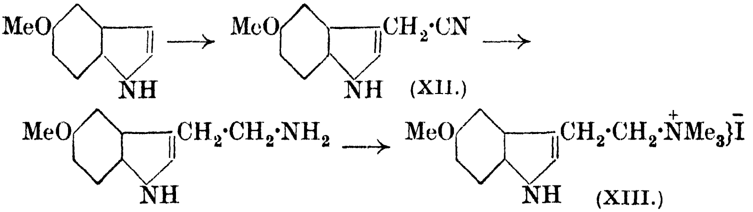
[25] (the late) W. H. Perkin, R. Robinson, and J. C. Smith, *J.*, 1934, 574; O. Achmatowicz and R. Robinson, *ibid.*, p. 581; L. H. Briggs and R. Robinson, *ibid.*, p. 590; (Miss) T. M. Reynolds and R. Robinson, *ibid.*, p. 592; B. K. Blount and R. Robinson, *ibid.*, p. 595; *A.*, 788.

[26] *Ber.*, 1931, **64**, [*B*], 2099; *A.*, 1931, 1310; *Ann. Reports*, 1931, **28**, 161.

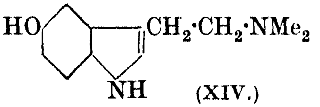
[27] H. Wieland, W. Konsand, and H. Mittasch, *Annalen*, 1934, **513**, 1; *A.*, 1232.

amino-group attached to one of two carbon atoms not forming part of the indole structure.

Biological considerations suggest a tryptophan structure, and, since the 2-position is free (positive Hopkins–Cole glyoxylic acid reaction), the hydroxyl group must be in position 4, 5, 6, or 7. Positions 4 and 7 may be excluded, for no natural indole derivatives are hydroxylated in these positions, whereas 5- and 6-hydroxylation is common (eseroline; harmine). The authors therefore synthesised derivatives of both (5- and 6-) types. Methylation of the known 6-methoxytryptamine with methyl iodide and thallium ethoxide gave a compound similar to the quaternary iodide obtained from bufotenine, but different from it. 5-Methoxyindole, treated first with methylmagnesium iodide and then with chloroacetonitrile,[28] gave (XII), which was reduced, the product being methylated with methyl iodide in presence of thallium ethoxide. The compound so obtained (XIII) was identical with *O*-methylbufotenine methiodide, from which it follows that bufotenine is (XIV) and bufotenidine is (XV).



(XII.) (XIII.)



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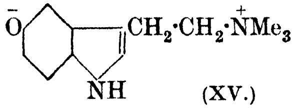

(XV.)

It is suggested that the statement of H. Jensen and K. K. Chen,[29] that the bufotenines from different species of toads are not identical, is incorrect, since it is now shown that the flavianate method of isolation leads to impure materials, *viz.*, to mixtures of varying proportions of bufotenine and bufotenidine with the base, $C_{12}H_{14}ON_2$, obtained [30] by removing the elements of sulphuric acid from bufothionine.

C. Schöpf and W. Braun [31] have isolated an "alkaloid," samandarine, $C_{19}H_{31}O_2N$, from the salamanders, *salamandra maculosa* and *s. atra*. The "samandatrine" extracted by Netolitzky [32] from

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[28] R. Majima and M. Kotake, *Ber.*, 1922, **55**, 3859; *A.*, 1923, i, 156.

[29] *Ber.*, 1932, **65**, [*B*], 1310; *A.*, 1932, 1142.

[30] H. Wieland and F. Vocke, *Annalen*, 1930, **481**, 215; *A.*, 1930, 1466.

[31] *Annalen*, 1934, **514**, 69; *A.*, 1935, 97.

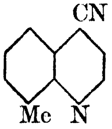
[32] *Arch. exp. Path. Pharm.*, 1904, **51**, 118; *A.*, 1904, i, 770.

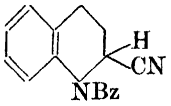
s. atra is shown to be identical with samandarine obtained either from Belgian or Spanish salamanders. Each Spanish salamander contains an average of 16·5 mg. of samandarine, the figures for the Belgian and Tyrolese species being 23·6 and 4·7 mg., respectively. Chemical investigation of samandarine has so far shown that it is probably a derivative of ethylene oxide, and contains a secondary carbinol group and an imino-group.

Stereochemistry of Heterocyclic Compounds.

O. Mumm and E. Herrendörfer[33] observed that, when quinoline was treated with a mixture of cyanogen bromide and hydrogen cyanide, a crystalline compound, $C_9H_7N(CN)_2$, was formed. This with alcoholic ammonia gave a crystalline isomeride. Continuation of this work[34] has given results of considerable interest and importance. Pairs of isomeric dicyanides were obtained with 3- and 6-methyl-, and 6-methoxy-quinoline, and with β-naphthaquinoline. *iso*Quinoline gave only one dicyanide, and 8-methylquinoline and α-naphthaquinoline gave none under the conditions employed for the preparation of the others. At higher temperatures these two compounds, and also 2-methyl- and 2-phenyl-quinoline, reacted, but gave, instead of the dicyanide, the nitrile of the corresponding 4-carboxylic acid, *e.g.*, (I). The reaction of quinoline derivatives with cyanogen bromide and hydrogen cyanide recalls the work of Reissert,[35] who found that quinoline, when treated with a mixture of aqueous potassium cyanide and benzoyl chloride, was converted into the nitrile (II), which gave quinoline-2-carboxylic acid in presence of mineral acids. Mumm and Ludwig regarded the two

(I.)





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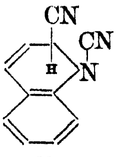

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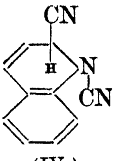
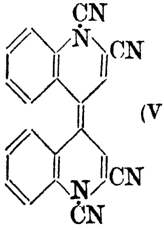


(IV.)



(V.)

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[33] *Ber.*, 1914, **47**, 758; *A.*, 1914, i, 574.

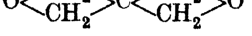
[34] O. Mumm and H. Ludwig, *Annalen*, 1934, **514**, 34; *A.*, 1935, 92.

[35] *Ber.*, 1905, **38**, 1603; *A.*, 1905, i, 472.

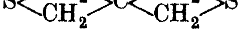
quinoline "dicyanides" as *cis–trans*-isomerides (III) and (IV) of a type not hitherto obtainable. Both isomerides with hydrochloric acid at 150° gave quinoline-2-carboxylic acid; both, when treated with iodine in chloroform solution, in presence of sodium acetate, gave 2-cyanoquinoline; and both were converted by iodine, in alcoholic pyridine solution, into the same apocyanine dye (V).

s-Dioxa*spiro*heptane (VI) and its thio-analogue (VII) have been prepared by H. J. Backer and K. J. Keuning.[36] Some evidence has been obtained that a disulphoxide of (VII) is capable of exhibiting optical activity.

(VI.)



$O<^{CH_2}_{CH_2}>C<^{CH_2}_{CH_2}>O$

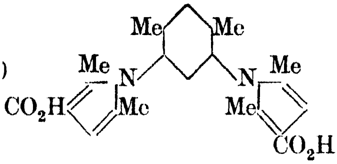


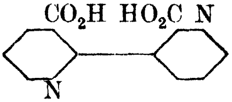
$S<^{CH_2}_{CH_2}>C<^{CH_2}_{CH_2}>S$

(VII.)

A dipyrrylbenzene (VIII) has been obtained[37] in *cis*- and *trans*-forms, and the latter has been resolved. The active forms are resistant to racemising influences.

(VIII.)



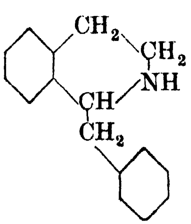


(IX.)

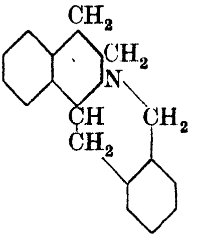
W. Brydowna[38] has effected the partial resolution of the strychnine and quinine salts of 2 : 3′-dipyridyl-2′ : 3-dicarboxylic acid (IX), but the acid itself was not obtained optically active.

The stereochemistry of such compounds is still in a very unsatisfactory condition, as virtually nothing is known of the molecular dimensions and configuration of such common ring compounds as pyrrole and pyridine.

W. Leithe[39] resolved *dl*-1-benzyl*iso*quinoline (X) with tartaric acid, and concluded that the specific rotation was ± 9°, in benzene solution. Repetition[40] of the resolution with bromocamphor-



(X.)



(XI.)

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[36] *Rec. trav. chim.*, 1934, **53**, 812; *A.*, 900; *ibid.*, 1933, **52**, 499; *A.*, 1933, 834.

[37] C. Chang and R. Adams, *J. Amer. Chem. Soc.*, 1934, **56**, 2089; *A.*, 1369.

[38] *Rocz. Chem.*, 1934, **14**, 304; *A.*, 1011.

[39] *Monatsh.*, 1929, **53–54**, 957; *A.*, 1929, 1461.

[40] *Ber.*, 1934, **67**, [*B*], 1261; *A.*, 908.

sulphonic acid gave the much higher rotation of — 72° for the *l*-base. The latter, when converted into tetrahydroprotoberberine (XI) by the method of E. Späth, F. Berger, and W. Kuntara,[41] gave a lævorotatory specimen of (XI) which, after crystallisation, was *optically pure*. This proves that the lævorotatory bases of the berberine class correspond to natural laudanosine (*l*-rotatory in carbon disulphide and *d*-rotatory in chloroform), which in turn corresponds to *l*-α-phenylethylamine.

A new chapter in stereochemistry has been opened in connexion with the configuration of heterocyclic rings. As recorded in these Reports,[42] E. Bergmann and M. Tschudnowsky [43] found that thianthren had the considerable dipole moment of 1·68 *D*, a fact only to be explained on the assumption that the thianthren molecule is folded. A redetermination of the dipole moment by G. M. Bennett and S. Glasstone [44] gave the value 1·5 *D*, and these authors pointed out that the valency bonds of sulphur in thianthren must therefore make an angle of less than 120° with one another. The corresponding angle in thianthren disulphoxide (XII) is not known, but H. Baw, G. M. Bennett, and (Miss) P. Dearns [45] have made a careful search for the third disulphoxide which should be capable of existence if the folded configuration of thianthren persists in the dioxides. The same authors have extended the work of K. Fries and W. Vogt,[46] by examining the products of oxidising various thianthrens. Whilst, however, 2 : 6-dichlorothianthren was shown to give rise to a monoxide, a monosulphone, two dioxides, a trioxide, and a disulphone, a third dioxide could not be detected, although the successful isolation of so many individuals clearly indicates the care with which the investigation was prosecuted. Similar results were obtained with 2 : 6-dimethyl- and 2 : 6-dimethoxy-thianthren : two disulphoxides were obtainable, but not a third.

A perhaps unexpected result was later obtained with diphenylene dioxide, the dipole moment of which was found to be zero.[47] It follows that the molecule of diphenylene dioxide must be planar, with an angle of about 120° between the oxygen bonds.

(Miss) M. S. Lesslie and E. E. Turner [48] point out that in a compound of the general formula (XIII), in which A and B are the same element, or are different, there is every reason to believe that the four lines joining the centres of A and B to the centres of the carbon atoms to which A and B are attached, will pass through the centre of X or of Y. This condition can be fulfilled even if the plane XAB is inclined, about the axis AB, to the plane YAB, as it is in thianthren.

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[41] *Ber.*, 1930, **63**, [*B*], 134; *A.*, 1930, 350.

[42] *Ann. Reports*, 1932, **29**, 185.

[43] *Ber.*, 1932, **65**, [*B*], 458; *A.*, 1932, 507.

[44] *J.*, 1934, 128; *A.*, 349.

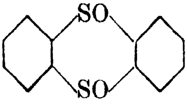
[45] *Ibid.*, p. 680; *A.*, 781.

[46] *Ber.*, 1911, **44**, 756; *A.*, 1911, i, 395.

[47] G. M. Bennett, D. P. Earp, and S. Glasstone, *J.*, 1934, 1179; *A.*, 1058.

[48] *Ibid.*, p. 1170; *A.*, 1118.

When A and B are not identical, it is still possible for XAB and YAB to be planes, and for these to be inclined to each other. The authors take the view that, when the atomic radii of A and B are markedly different, the stability of a folded structure will be greater. It is shown by calculation that, when A is an oxygen atom (radius, 0·66 Å.) and B is a tervalent arsenic atom (radius, 1·21 Å.), the most probable configuration of such a system is one in which the angle between the planes XAB and YAB is between 150° and 180°. An attempt to test this view resulted in the optical resolution of 10-methylphenoxarsine-2-carboxylic acid (XIV), the enantiomorphic forms of which possessed very high optical stability. This fact makes it very improbable that the observed activity is due to the presence of an " asymmetric tervalent arsenic atom," but further work should clear up this matter. In view of the results obtained by O. Mumm and H. Ludwig,[34] the whole subject needs careful consideration.



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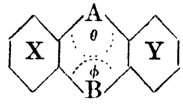

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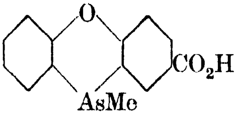

(XIV.)

From another quarter,[49] a claim has been made that tervalent arsenic can give rise to optical activity, but [48] the evidence put forward requires considerable amplification.

The discovery of molecular dissymmetry in the phenoxarsine series makes it almost certain that a large number of analogous structures will be resolved. It will be of interest to know whether such activity occurs in substances of natural origin. Possibly molecular dissymmetry of the new type, like that due to restricted rotation, is not made use of by nature.

E. E. TURNER.

[49] C. F. H. Allen, F. B. Wells, and C. V. Wilson, *J. Amer. Chem. Soc.*, 1934, **56**, 233; *A.*, 312.

ANALYTICAL CHEMISTRY.

1. GENERAL METHODS, ETC.

IN this Report it has again been considered desirable to present short monographs on some branches of analytical chemistry, where much work has been carried out recently and the time seems fitting for the presentation of a connected summary of the advances made.

Adsorption on Precipitates in Gravimetric Determinations.—In quantitative determinations depending upon the precipitation of a definite compound, it is essential to know whether the precipitate is truly the desired compound. It is well known that adsorption effects, due to alkalis or to the difficulty of eliminating an anion completely (as in the case of the sulphate ion in precipitating aluminium hydroxide), may introduce serious errors if not recognised and dealt with. Precipitation of barium sulphate under various conditions is, perhaps, the best known example of co-precipitation of cations to a greater or less extent according to the nature of the cation. The general question of contamination of crystalline solid systems, whether obtained by precipitation from solutions, from melts, or by condensation from vapours, forms the subject of an important series of papers, now summarised conveniently.[1] In whatever manner produced, the crystalline precipitate is formed discontinuously. The resulting crystal precipitates may therefore consist of "growth" conglomerates holding adsorbed impurities deposited regularly, or may contain ions of the same kind as that of the lattice but as foreign molecules either adsorbed in certain layers or in solid solution. Impurities will be more serious when the crystal has a mosaic or "amorphous" structure. Quantitatively, these effects will be manifested by the departure of the precipitates from the strict stoicheiometric composition of the desired compound, arising, for example, from the inclusion of foreign barium salts (or sulphates of other metals) in barium sulphate, and of other sulphides (or salts) in those cases where a quantitative precipitation is made by way of a sulphide.

While these views are probably sound in general, a particular study of adsorptive properties of barium sulphate precipitates when croceine scarlet 3BX is employed for staining the crystals, showed that the greatest adsorption occurred with irregular crystals.

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[1] D. Balarew, *Z. anal. Chem.*, 1934, **96**, 81; *A.*, 267.

Orthorhombic crystals take up little dye, and that is distributed locally within the crystal.[2] Adsorption is considered to take place during the brief periods which may occur when a change in the manner of crystal growth takes place. It is suggested that least adsorption in the gravimetric precipitations of barium sulphate will result if conditions are chosen so that the precipitate consists, as far as possible, of perfect orthorhombic crystals.

It is interesting to consider how it is possible to arrive at departures from true stoicheiometric relations in a neutral salt deposited from an electrically neutral mother-liquor. A likely explanation is that some cations (or anions) of the crystal and a corresponding number of anions (or cations), *e.g.*, those derived from the mother-liquor, are deformed in such a way as to form electrically neutral groups externally, but not necessarily neutral atoms or radicals, in so far as the electronic arrangements of the atoms or groups themselves are concerned. It follows that care must be exercised in the final treatment quantitatively of any precipitate to ensure that the foreign substances are either expelled during an ignition or removed so far as may be by suitable treatment of the precipitates. Fortunately, there are many cases in practice where the conditions described above do not introduce serious errors in ordinary cases, but the possibility of structural contamination of precipitates cannot be ignored in very accurate work.

Radioactive Methods in Technical Problems.[3]—An interesting review of methods of investigating certain problems by the use of radioactive processes has been made. *X*-Ray examination has shown that active charcoal occurs in the form of microcrystalline graphite, and it has been assumed that adsorption occurs at the prism faces or sides of the graphite crystals where free carbon valencies may be expected to occur, and not on those faces of graphite crystals which form the bases. A direct demonstration of this is obtained when a small graphite flake is immersed in an atmosphere containing radon. On placing the flake on a photographic plate, marked blackening is found due to α-particles arising from radon adsorbed in the prism surfaces bounding the edges of the flake, but very little effect is observed where the base of the flake rests on the plate. The fact that small quantities of various admixtures in a substance can often be adsorbed completely by impurities contained therein (*e.g.*, in slag inclusions of metals) may probably account for Tammann's observations that when alloys containing ordinary lead, to the extent of about 1% in tin, or 5% in bismuth, have thorium-*B* added to them by a process of melting, the radioactive material is found almost exclusively at the edges of the crystal grains and not uniformly distributed throughout the alloy. This has nothing to do with the radioactivity of the lead isotope, Th-*B*, for it was found by H. Käding and N. Riehl that if lead charged with Th-*B* were melted with tin, radioactive lead was distributed uniformly throughout the alloy. This method of examining alloys for crystal grain and slag inclusions agrees with the results obtained by etching the metal with various reagents.

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[2] E. G. R. Ardagh, R. E. Richardson, L. A. Richardson, and L. M. Humber, *J. Soc. Chem. Ind.*, 1934, **53**, 1035T.

[3] H. Käding and N. Riehl, *Angew. Chem.*, 1934, **47**, 263; *A.*, 617.

Von Hevesy and Paneth's well-known method of radioactive indicators, whereby a radioactive isotope can be deposited with its inactive isotopic element, is not confined to these elements. It is necessary that the element under examination should be capable of forming an insoluble compound with some other element which has a radioactive isotope. This points the way to the detection of traces of elements which have no radioactive isotopes.

X-*Ray Methods in Chemical Analysis.*—A critical study of the methods and of the variables peculiar to the apparatus was made with a Siegbahn type of apparatus.[4] Special attention was directed to the evaluation of the spectrograms. The method employed was to hammer the sample of powder into the surface of a copper anticathode, and to ensure uniformity of emission of electrons from a flat platinum spiral coated with barium oxide–strontium oxide powder, the filament being wound tightly and regularly, and carefully centred in the electron shield. By visual observation of the fluorescence, the evenness of the stream of electrons over the " focal " area of the anticathode was observed and adjusted. Rocking of the calcite diffracting crystal could also be applied to correct any slight irregularities in the distribution of electrons. When all precautions were taken for regulating the voltage, time of exposure, development of plates, and general mechanical procedure, values from the plates could be trusted to within 5%. It was shown that only those analyses which were made under strictly comparable conditions could have any claim to accuracy, and that an absolute method of analysis should then be possible. Lines arising from a single element would be utilised in each determination, by comparison with a set of lines of the element obtained on the same photographic plate with various proportions of the element in a mixture similar to that under test. The results are set out in a graph showing log (time of exposure)–density, since this is a more suitable function for determining the proportion of the element from a measurement of the density of the plate than that usually adopted in photography of the visual spectrum, *viz.*, log intensity–density. The method proposed is apparently more widely applicable than that of Laby, which is, in general, restricted to elements of near atomic numbers.

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[4] E. Wainer, *J. Amer. Chem. Soc.*, 1934, **56**, 1653; *A.*, 1084.

The question of the sensitivity of the *X*-ray method of chemical analysis has been re-examined, and it is reported that for certain alloys, metals can be detected by cathode-ray excitation down to 1 part in 10^5, and in powders elements can be found to the extent of about 1 part in 2×10^4, particularly if the shorter wave-lengths are employed.[5] It is clear from a perusal of recent work on the application of *X*-ray methods of analysis that such methods will take their place side by side with spectrographic methods, and, indeed, will replace them in many cases, since the *X*-ray spectrograms are so much simpler and easier to interpret.

Spectrographic Methods.—Although no striking new features are reported during the year, a few modifications of accepted practice may be indicated. When a substance which is being excited electrically to the state of emission is simultaneously heated, the length, width, and intensity of some of the spectral lines may alter. By selecting a line of an element in a mineral under investigation, susceptible to such effects, and photographing it at fixed intervals on a plate which moves vertically at a fixed rate, the variation in the length, breadth, and intensity of the line is ascertained. This forms the basis of a method for estimating the element to which the line is due.[6]

An adaptation of the visual flame spectrum enables a determination of certain cations—alkali metals, alkali earths, and thallium—to be made with an accuracy of about ± 10%. The concentration of the solutions varied from 2 or 3% to 1×10^{-4}%, and even less in some cases. The procedure is to atomise a few c.c. of the solution in a Lundegårdh flame atomiser burning acetylene. In front of the slit of the spectroscope there is placed a rectangular cell of plane parallel glass sides, about 20 cm. long and 2 cm. wide, divided diagonally by means of a plane parallel glass septum. One half of the cell contains water and the other half a solution of copper sulphate or potassium permanganate to act as light filters. The critical strength of solution for various concentrations of the element under examination at which certain spectrum lines vanish is ascertained, and curves connecting the logarithm of percentage concentration with thickness of layer of filter are drawn for each element. Since other cations may introduce errors, the solution under test must be compared with one containing the disturbing element.[7] The method is clearly capable of extended application. In dealing with the sparking of solutions, the apparatus devised by F. Twyman and C. S. Hitchen [8] has been found available for the spectroscopic determination of Nb, Be, Ti, V, W, Mo, Cr, and Pb, when used with the logarithmic sector. Concentrations as low as $5 \times 10^{-4}\%$ of beryllium can be estimated with an error no greater than 5%.[9]

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[5] A. Faessler, *Z. Physik*, 1934, **88**, 342; *A.*, 617; R. Glocker, *Metallwirt.*, 1933, **12**, 599; *A.*, 1934, 979.

[6] A. Batim, *Compt. rend.*, 1934, **198**, 566; *A.*, 380.

In view of the importance of a knowledge of the content of fluorine in water supplies, it is interesting to note the rapid spectroscopic method now available [10] either visually or photographically. This depends on the observation of the head of the blue-green CaF band at λ5291. Where the water residue—about 12·5 mg. is taken—is essentially calcium and magnesium, the visual method is available. The residue is placed in the cavity of a cored graphite electrode, impregnated with calcium chloride, and an arc carrying about 15 amps. is struck. This arc shows the λ5291 fluoride band which persists for various times according to the proportion of fluoride in the water residue, but it disappears when all the fluoride has volatilised. By plotting the percentage of fluorine in the residue against the number of seconds before disappearance of the band head, a curve can be drawn from standard mixtures, enabling the quantity of fluorine in the mineral residue from the water to be read off. When the water residue is mostly saline, the visual method fails and the spectrographic method is necessary. In this case, the arc is kept burning for one minute, this being sufficient to volatilise all the fluorine likely to be found in waters generally. The intensity of the band head is compared with that of known standards in the usual way. Quantities of fluorine down to 0·05 part per million can be estimated.

Two other spectrophotometric determinations may be considered here. Aluminium may be detected by means of the lakes it forms with a number of dyestuffs, but the great majority of these are not sensitive enough to estimate 1 or 2γ of metal. Eriochrome-cyanin R does, however, detect as little as $0{\cdot}5\gamma$, and even 1γ can be found when mixed with as much as 100 times the quantity of iron, chromium, or manganese. For quantitative work, advantage is taken of the fact the aluminium lake has its maximum absorption about λ530 mμ in the green part of the spectrum, whereas that of the original solution is in the violet-blue region. The position of the band maximum is affected by varying p_H, and the aluminium solution containing dye is therefore held at p_H 6 by means of a buffer mixture of acetic acid with sodium and ammonium acetates. The extinction coefficient of the buffered solution of aluminium and dyestuff at λ531 mμ is measured, and this gives an estimate of the aluminium content of the solution. As an example, 10γ of the metal per 100 c.c. gives an extinction coefficient of about 0·2 in the conditions laid down.[11] This procedure of monochromatic spectrophotometric determination is of fairly wide application both visually and photographically.

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[7] A. K. Russanov, *Z. anal. Chem.*, 1934, **98**, 335; *A.*, 1190; H. Lundegårdh, "Die Quantitative Spektralanalyse der Elemente" (Jena, 1929).

[8] *Proc. Roy. Soc.*, 1931, [*A*], **133**, 72; *A.*, 1931, 1260.

[9] W. R. Brode and J. G. Steed, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 157; *A.*, 748.

[10] A. W. Petrey, *ibid.*, p. 343; *A.*, 1189.

In addition to the uses of diacetyl as a reagent, it has found application for imparting aroma to butter in those cases where the minute proportion present in the butter naturally has been reduced back to acetylmethylcarbinol from which it is presumed to be formed in fresh butter. In these circumstances, it becomes of interest to ascertain whether it is possible to detect addition, when this is more than might be found normally, *i.e.*, about 0·0005% (the true maximum in fresh butter is really unknown). One test is to convert the diacetyl into dimethylglyoxime and determine it colorimetrically by means of the nickel compound. An alternative method has been proposed [12] from the estimation of the extinction coefficients of the bands in the regions 4200 and 2870 Å. The diacetyl is distilled out of the butter by means of alcohol, and the distillate is examined spectrophotometrically and compared with curves drawn from known concentrations in 88% alcohol by volume. Now, reduction of the diacetyl may well proceed as far as $\beta\gamma$-butyleneglycol, and it is known that certain organisms bring about the formation of acetylmethylcarbinol. Further, during the oxidation of the alcohol, when butter becomes stale, small quantities of the butter itself are broken up during the steps leading to rancidity, and it is probable that volatile substances are formed which will distil over with the diacetyl. What effect these would have on the determination of the extinction coefficient is unknown. Until further information on these matters is available, it would appear preferable to rely on the nickel test for diacetyl, rather than on the spectroscopic determination.

Of the various uses for photoelectric colorimetry, the arrangement of B. Lange [13] has been applied to the direct examination of water for iron, manganese, and phenol. The iron is determined from the depth of colour of the thiocyanate, and the manganese from that of permanganate. Phenol is estimated by the blue colour given by Folin and Dennis's reagent, phosphomolybdic acid. It is not clear why the authors have not, in this case, used one of the dyes produced by coupling the phenol with a diazonium compound. The type of instrument used is available for the nephelometric determination of sulphates as barium sulphate and lead as lead sulphide, in both cases with the aid of a stabilising colloid such as gum arabic.

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[11] F. Alten, H. Weiland, and E. Knippenberg, *Z. anal. Chem.*, 1934, **96**, 91; *A.*, 271.

[12] H. Mohler and F. Almasy, *ibid.*, p. 399; *A.*, 635.

[13] *Chem. Fabr.*, 1933, 457; *A.*, 1933, 44; E. Naumann and K. Naumann, *Z. anal. Chem.*, 1934, **97**, 81; *A.*, 744.

Of the numerous fluorescence reactions described, one may be specially mentioned, *viz.*, the orange-yellow fluorescence shown in ultra-violet light by boric acid solutions to which cochineal extract is added.[14] The solution must be brought between p_H 5·8 and 6·9, and buffered with equimolecular mixtures of KH_2PO_4 and $Na_2HPO_4,2H_2O$. The test is four or five times as sensitive as that given by turmeric. If necessary, carbonates should be removed, since they interfere with the fluorescence, but some other anions are without effect. Heavy metals in general prevent the formation of the specific fluorescence colours, and certain cations develop a differently coloured fluorescence. We have no doubt it would be possible to distil off the boric acid by means of methyl alcohol in the well-known manner and so separate it from the cations, an advantage of some importance since it is claimed that the fluorescence with cochineal extract is specific for boric acid in the conditions described.

Interferometric and Other Measurements of Refractivity.—Optical interferometers have been used frequently to determine differences in refractivity in very dilute solutions or in binary mixtures of gases, or for a constant gas mixture (*e.g.*, air) and an impurity. Organic vapours in air can thus be determined if the refractive index of the vapour is known, or calibration curves are determined from known mixtures.[15] In the same way, the difference in refractivity between ordinary water and a concentrate containing more heavy water is a means of determining the proportion of heavy water rapidly and with an accuracy limited by the amount of water available and the length of observation cell. With interferometers employing white light and an achromatic fringe as the zero of a drum reading, it is necessary to take account of one serious error which may arise from the different dispersions of the glass compensator plates, the solution, and the standard water.[16] Hence it is best to calibrate the drum of the instrument in such a manner as to give readings of the

[14] L. Szebellédy and H. Gaal, *Z. anal. Chem.*, 1934, **98**, 255; *A.*, 1190.

[15] H. Schildwächter, *Petroleum*, 1934, **30**, No. 11, 1; *A.*, 619.

[16] R. H. Crist, G. M. Murphy, and H. C. Urey, *J. Chem. Physics*, 1934, **2**, 112; *A.*, 618.

apparent differences of refractive index against the corresponding differences in specific gravity. When all precautions are taken, the accuracy with a cell only 4 cm. in length is about 0·01% of heavy water.

Mention may be made of refractivity measurement for distinguishing between different series of hydrocarbons.[17] The so-called specific dispersion is utilised; that is, the difference in refractive indices for the Hg line λ4358 and H_α λ6563, divided by the density at 20°. As an example, the value of this quantity × 10^4 for paraffins and naphthenes is about 157, while for olefins and unsaturated cyclic hydrocarbons containing one double bond it is 185.

Dielectric Constant in Analytical Determinations.—From time to time determinations of dielectric constant have been suggested—and sometimes applied—as an analytical method. It is obvious that, given reliable means of ascertaining this physical constant, we would have an additional means of determining composition. For example, water in solids or certain liquids could be determined with some accuracy, or mixtures such as acetone or alcohol in benzene. The present position is that commercial apparatus is available for making measurements with solids or liquids, and any " wireless " enthusiast could readily fit up an accurate apparatus. We have found that with certain powders, the dielectric constant, or permittivity, varies directly with the proportion of water, but that the permittivity calculated on the assumption that the powders may be regarded as a mixed dielectric consisting of anhydrous solid, water, and air, is not that found experimentally, although the slopes of the lines are nearly identical.[18] It is further to be noted that, if salts are present in the powder, the curve for percentage of water–dielectric constant may suddenly depart from a straight line with the higher proportions of water. Again, the method may be relatively insensitive as an analytical procedure with liquids whose dielectric constants are close together, *e.g.*, carbon tetrachloride and benzol. In such cases, the refractive index or even the density is more accurate. Nevertheless, the scope of the technical utility of determinations of dielectric constant has recently been widened [19] by the use of dioxan as a solvent or dehydrating liquid. This substance has $\varepsilon = 2{\cdot}22$ at 20°, a value not far removed from other liquids which are free from dipoles, *e.g.*, carbon tetrachloride, for which ε at 20° is 2·24. Its solvent power for organic liquids and for water renders it specially valuable, since its degree of hygroscopicity may be varied considerably by addition of non-hygroscopic liquids such as paraffin oil. To illustrate the possibilities of the use of dioxan, it may be pointed out that the addition of 1% of water increases the dielectric constant by about 12%, a substantial alteration, and capable of ready and rapid measurement in modern apparatus. Amongst other investigations carried out with dioxan may be mentioned the determination of adsorption (or desorption) equilibrium of surfaces.[19] Dry dioxan is poured over the anhydrous powder (*e.g.*, a starch flour), a little water is added to the mixture, and the dielectric constant is determined on a portion of the filtered liquid from time to time, the determination occupying less than one minute. With starch, a rapid adsorption occurred, followed by a slow adsorption lasting many hours. Presumably this kind of investigation requires the dioxan to be present in very large excess.

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[17] A. L. Ward and W. H. Fulweiler, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 396.

[18] Unpublished work. [19] L. Ebert, *Angew. Chem.*, 1934, **47**, 305.

Dioxan mixed with diluents (paraffin oil) to reduce its power of taking up water may be employed for the rapid determination of water in powders, the quantity of diluent used depending upon the adsorptive power of the powder, *e.g.*, sand, active charcoal, cement. Further, the application of the method is not limited to water, but by selection of suitable diluents of higher dielectric constant, such as the alcohols, it is possible to determine other adsorbed, or mechanically held, substances of the nature of grease or solvent. It seems likely that the results obtained will be of the same order of accuracy as that of a refractometric method, but are not likely to reach the sensitivity obtained by the dipping refractometer, which is also very rapid and needs but little liquid for test.

Analytical Methods in Gas Analysis.—A few of the more important discussions may be considered in relation to their practical bearing. The accuracy of vapour–liquid equilibria of binary mixtures which depart from the ideal laws of solutions is discussed in relation to the Duhem–Margules equation $d\log p_1/d\log p_2 = -(1-x)/x$, in which x and $(1-x)$ are the molecular fractions of the components, x being the more volatile, and p_1, p_2 are the corresponding partial pressures at some given temperature.[20] This formula may be transformed into a very similar one by using the "activity coefficients" as defined by Lewis and Randall ("Thermodynamics"). Developments of the formulæ then lead to criteria by which the accuracy of experimental data on partial vapour pressures may be tested rigidly.

Whenever rubber tubing and stopcock grease have to be used in the analysis of gases, two possibilities of error may arise and should be borne in mind.[21] Hydrocarbons and carbon dioxide may be absorbed by the rubber and grease, and some of these gases may be given up when the apparatus is used again. Sometimes the

[20] H. A. Beatty and G. Calingaert, *Ind. Eng. Chem.*, 1934, **26**, 904.

[21] J. R. Branham, *Bur. Stand. J. Res.*, 1934, **12**, 353; *A.*, 626.

error is large, and if rubber cannot be avoided, it is necessary to ascertain the losses by examining synthetic mixtures. Apart from this source of error, there is the possibility of serious misinterpretation of results obtained by explosion of a gaseous hydrocarbon with commercial oxygen (and even with pure oxygen) when the analysis is made by way of the determination of the contraction in volume of the gas and oxygen or air mixture.[22] If the results for an unknown mixture of pure ethane and air are computed as in an ordinary gas analysis, it is shown that substantial proportions of methane may be reported from an interpretation of the results when none is present. Better results are obtained by slow combustion of the gaseous mixture. Attempts were made to shorten the time of analysis by more rapid combustion, but it appeared that the experiments were more in the nature of stimulants to the operator because of the possibility of disaster to the apparatus (and operator); so far as they went, however, the results were similar to those obtained by direct explosion.

Small quantities of oxygen of the order of 0·07% in gas mixtures may be determined by absorbing it in fresh alkaline pyrogallol and matching the colour produced against *N*/10-iodine solution. Hydrocarbons and oxides of carbon do not interfere with this determination.[23] An exhaustive study of the accuracy of determining oxygen by absorption with phosphorus has been carried out.[24] It is suggested that, in the process of absorption, some intermediate form of oxygen other than ozone is present, this assumption being necessary to account for the observed oxidation of some hydrogen and carbon monoxide when these gases are present with oxygen in the presence of moist phosphorus. It does not seem to the Reporter to be necessary to assume the presence of forms of oxygen other than that of atomic, or an activated form of molecular, oxygen at the surface of the phosphorus. The existence of oxygen in energy states as well as that of the normal gaseous state is well-enough established and would be expected at the surface of phosphorus. In this sense it may be claimed that an intermediate substance[25] is present in the reacting mixture. The fact that certain reactive organic molecules inhibit the oxidation of phosphorus is also understood if the effect of such substances is to form a molecular layer on the surface of the phosphorus, or to take up the energy of activated oxygen without combination. It is interesting to speculate whether considerations of the oxidation of hydrogen at the surface of the phosphorus do not really afford an explanation of the striking result that the extent of oxidation of hydrogen varies inversely as the proportion of oxygen in the gas under test.[26]

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[22] J. R. Branham and M. Shepherd, *Bur. Stand. J. Res.*, 1934, **13**, 377.

[23] H. R. Ambler, *Analyst*, 1934, **59**, 14; *A.*, 268.

[24] *Idem*, *ibid.*, p. 593; *A.*, 1186.

[25] *Ibid.*, p. 605.

In view of the increasing use of carbon monoxide in industry, it is important to know the purity of the commercial gas. A paper [27] dealing with the analysis of this gas is therefore timely. Nitrogen, hydrogen, and methane were determined, and small proportions were found. Iron carbonyl was also found in proportions varying from $1 \times 10^{-4}\%$ to $1{\cdot}5 \times 10^{-3}\%$, the quantity increasing with the time the gas has been stored in the cylinder.

A further study of the use of platinised silica gel in gas analysis has been undertaken,[28] dealing in this case with the oxidation of methane, ethane, propane, and butane. Oxidation does not result with methane at 350°, ethane at 230°, propane at 130°, or butane at 120°, but occurs at some 20—25° above these temperatures, although oxidation was not complete even at 400°. Since hydrogen and carbon monoxide can be quantitatively oxidised over the catalyst at 300°, it follows that these two gases can be determined in the presence of methane, but not when the other hydrocarbons are present, for they are likewise oxidised at this temperature. In this connexion, earlier work on the temperatures for oxidation over copper oxide should be studied.[29]

A possible source of error in accurate work depending upon manometric measurements arises from an uncertainty in determining capillary depressions of mercury in cylindrical glass tubes of the ordinary kind, because of a refraction error due to the glass. In order to eliminate these errors, thin-walled tubes are necessary for the manometers, and a special design has been used.[30] The relationship between capillary depression and height of meniscus for tubes of 10—19 mm. diameter and meniscus heights of 0—1·8 mm. has been worked out and tabulated. The results are probably the most accurate available.

Volumetric Standards.—Search for suitable secondary standards for volumetric analysis reveals certain novelties. Furoic acid can be purified easily by crystallisation and sublimation, the acid of m. p. 131° then being available as a pure material.[31] When great accuracy is desired, and in all those cases where trustworthy volumetric solutions are required, the standardisation of hydrochloric acid by pure silver is indicated and has been employed in many laboratories. This is stressed in a recent paper[32] in which detailed instructions are given for the use of silver as a primary standard. An unusual standard material for acidimetry is $3CdSO_4,8H_2O$, a crystalline substance readily obtained pure. This salt is dissolved in water and electrolysed over a mercury cathode, thereby giving a solution containing the stoicheiometric quantity of sulphuric acid, which is available for the standardisation of an alkali.[33]

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[26] H. R. Ambler, *Analyst*, 1934, **59**, 596.

[27] H. R. Ambler and T. C. Sutton, *ibid.*, p. 809.

[28] K. A. Kobe and E. B. Brookbank, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 35.

[29] J. C. King and L. J. Edgcombe, *Dept. Sci. Ind. Fuel Res.*, 1931, Tech. Paper No. 33.

[30] W. Cawood and H. S. Patterson, *Trans. Faraday Soc.*, 1933, **29**, 514.

[31] H. B. Kellog and A. M. Kellog, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 251.

Comparison and Indicator Electrodes.—Silver halides, on silver or fused on to platinum wires, can be employed for comparison electrodes in potential measurements, or if combined with platinum or antimony electrodes, will function as indicator electrodes.[34] For stability in solutions to be titrated, the liquids should be treated with sodium chloride or with silver nitrate or sulphate. In precipitation reactions with phosphate, chromate, and oxalate, these electrodes are unsuitable because the solubility of the compounds of silver precipitated is too high. A silver sulphide electrode can be used advantageously for sulphide precipitations, as with zinc determinations, or even for cyanometric titrations. For example, nickel in steel can be determined with a silver sulphide electrode, whereas a silver electrode fails on account of oxidation effects.

Antimony sulphide electrodes have been prepared for p_H measurements and are found to be available in the p_H range 2—10 with an accuracy of ± 0·05 unit. The electrodes are best prepared by heating antimony electrodes in 0·3*N*-nitric acid, and saturating the solution with hydrogen sulphide, in which the treated electrodes are stored until required.[35] Other methods of preparing the sulphide coating did not give such good electrodes. The liquid to be measured might contain starch, sugar, or nitrate ions without affecting the accuracy, but hydroxy-acids, such as tartaric, render the electrode useless; but this applies equally to the antimony oxide electrode. Although strongly alkaline solutions remove the sulphide film, the electrode still functions. J. J. F.

2. General Analytical Determinations.

In the determination of metals by precipitation with 8-hydroxyquinoline, followed by titration, it sometimes happens that the end-point is obscured by the formation of a brown cloudiness; this may be remedied by the addition of carbon disulphide to the solution before adding the potassium iodide.[1] Potentiometrically, this bromination may be followed in 10% hydrochloric acid, preferably at 50—55°; above 70° reaction is not stoicheiometric.[2] The precipitates obtained in acetic acid solution from thorium and uranyl salts with oxine are additive compounds containing one molecule of the hydroxyquinoline. They are stable at 100°, but when heated at higher temperatures, the oxine is expelled; the residues may be reconverted into their original form and colour, *e.g.*, by careful warming with oxine solution.[3] The vanadium compound $V_2O_3(C_9H_6ON)_4$ may be dried at 100° and weighed; precipitation in this form has been applied to steel analysis. The molybdenum complex is insoluble in dilute acetic acid.[4] Zinc may be determined in the presence of uranium by precipitation with oxine from alkaline tartrate or alkaline malate solution.[5] In the separation of iron and aluminium from beryllium with oxine, the addition of oxalic acid may lead to error.[6] In mixtures of iron, aluminium, calcium, and magnesium, the last is precipitated with oxine, after removal of the others, and then determined colorimetrically by coupling with diazotised sulphanilic acid, comparison being made with similarly treated standards.[7] The aluminium in such a mixture may be determined in a similar manner.[8] Accuracy to 1% for 1 mg. of magnesium is claimed for a micro-modification of Berg's volumetric method.[9] For the determination of copper by means of 5 : 7-dibromo-8-hydroxyquinoline the procedure of L. W. Haase [10] is preferred.[11]

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[32] C. W. Foulk and L. A. Pappenhagen, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 430.

[33] S. E. Q. Ashley and G. A. Hulett, *J. Amer. Chem. Soc.*, 1934, **56**, 1275.

[34] W. Hiltner, *Z. anal. Chem.*, 1933, **95**, 37; *A.*, 1934, 48.

[35] T. R. Ball, W. B. Schmidt, and K. S. Bergstresser, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 60; *A.*, 267.

Certain azo-derivatives of hydroxyquinoline are of value in detecting mercury(ic), palladium, and molybdenum (as $MoOCl_5''$) under specified conditions.[12]

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[1] H. R. Fleck, F. J. Greenane, and A. M. Ward, *Analyst*, 1934, **59**, 325; *A.*, 791.

[2] J. A. Atanasiu and A. J. Velculescu, *Z. anal. Chem.*, 1934, **97**, 102; *A.*, 791.

[3] F. J. Frere, *J. Amer. Chem. Soc.*, 1933, **55**, 4362; *A.*, 1934, 82.

[4] S. L. Tzinberg, *Zavod. Lab.*, 1933, No. 1, 18; *A.*, 1934, 1193.

[5] W. R. Wiggins and C. E. Wood, *J. Soc. Chem. Ind.*, 1934, **53**, 254T; *A.*, 1085.

[6] V. M. Zvenigorodskaja and T. N. Smirnova, *Z. anal. Chem.*, 1934, **97**, 323; *A.*, 982.

[7] F. Alten, H. Weiland, and B. Kurmies, *Angew. Chem.*, 1933, **46**, 697; *A.*, 1933, 1262.

[8] F. Alten, H. Weiland, and H. Loofman, *ibid.*, p. 668; *A.*, 1933, 1263.

[9] G. Glomaud, *J. Pharm. Chim.*, 1934, [viii], **19**, 14; *A.*, 270.

[10] *Z. anal. Chem.*, 1929, **78**, 113; *A.*, 1929, 1159.

[11] J. V. Dubský and J. Chytil, *Chem. Listy*, 1934, **28**, 6; *A.*, 382.

[12] G. Gutzeit and R. Monnier, *Helv. Chim. Acta*, 1933, **16**, 478; *A.*, 1933, 732; cf. *Ann. Reports*, 1933, **30**, 281.

With salts of gold and silver, tri(hydroxyethyl)amine forms metallic mirrors, and with those of manganese, nickel, and cobalt, characteristic coloured soluble complex compounds;[13] this base also precipitates tin from an ammonium carbonate solution of tin and antimony in their higher state of oxidation.[14]

The behaviour of bismuth with sulphur-containing reagents has been investigated, *e.g.*, alkali thiocyanates,[15] thiourea,[16] dimercaptothiodiazole,[17] 2-thiol-5-thio-4-phenyl-3 : 4-diazolone,[18] and numerous others.[19] Dimercaptothiodiazole may be used for the separation of copper and lead from various other metals.[20] Bismuth is extracted from most metals by a solution of diphenylthiocarbazone in chloroform.[21]

The metals which form insoluble pyridine thiocyanates may be determined indirectly by measuring the thiocyanate in the filtrate; this may be effected potentiometrically [22] or by ordinary volumetric methods.[23] The precipitation of mercury as $[\mathrm{Cu\ en_2}][\mathrm{HgI_4}]$, which serves to separate this metal from members of the hydrogen sulphide and the ammonium sulphide group,[24] may be followed potentiometrically.[25]

The perchlorate and picrate of methylene-blue are soluble in chloroform; this property may be applied to the determination of methylene-blue and picric acid [26] and of potassium, after precipitation as perchlorate or picrate.[27]

With many metals quinaldinic acid forms salts, normal or basic, of varying solubility in acids; [28] manganese is quantitatively precipitated from not too dilute neutral solution as anthranilate.[29] Precipitation of copper as oxalate with ammonia and oxalic acid is a good means of separating it from many other metals.[30] Iron, aluminium, and chromium are separated quantitatively from other metals of the third group by means of ammonium benzoate.[31] A scheme of qualitative analysis of the common metals of the ammonium sulphide group utilising organic reagents has been worked out.[32]

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[13] E. Jaffe, *Ann. Chim. appl.*, 1932, **22**, 737; *A.*, 1933, 246; *Ind. chim.*, 1934, **9**, 151; *A.*, 396; F. Garelli and A. Tettamanzi, *ibid.*, 1933, **8**, 577; *A.*, 1933, 813.

[14] Raymond, *Compt. rend.*, 1934, **198**, 1609; *A.*, 747.

[15] E. Tommila, *Suomen Kem.*, 1934, **7**, [*B*], 79; *A.*, 502.

[16] C. Mahr, *Z. anal. Chem.*, 1934, **97**, 96; *A.*, 748.

[17] J. V. Dubský and A. Okáč, *ibid.*, 1934, **96**, 267; *A.*, 502.

[18] J. V. Dubský and J. Trtílek, *ibid.*, p. 412; *A.*, 622.

[19] J. V. Dubský, A. Okáč, B. Okáč, and J. Trtílek, *ibid.*, **98**, 184; *A.*, 1193.

[20] J. Gupta, *J. Indian Chem. Soc.*, 1934, **11**, 403; *A.*, 982.

[21] L. A. Haddock, *Analyst*, 1934, **59**, 163; *A.*, 502.

[22] G. Spacu and P. Spacu, *Z. anal. Chem.*, 1934, **96**, 270; **97**, 99, 192, 263; *A.*, 502, 746, 747, 857.

[23] G. Spacu and M. Kuraš, *ibid.*, **99**, 26; *Bul. Soc. Ştiinţe Cluj*, 1934, **7**, 377; *A.*, 1323.

[24] G. Spacu and G. Suciu, *ibid.*, p. 183; *A.*, 270.

[25] G. Spacu and I. G. Murgulescu, *Z. anal. Chem.*, 1934, **96**, 109; *A.*, 270.

[26] A. Bolliger, *J. Proc. Roy. Soc. New South Wales*, 1933, **67**, 240; *A.*, 1017.

[27] *Idem*, *Z. anal. Chem.*, 1933, **94**, 403; *A.*, 47; *J. Biol. Chem.*, 1934, **107**, 229; *A.*, 1332.

[28] P. Rây and M. K. Bose, *Z. anal. Chem.*, 1933, **95**, 400; *A.*, 270.

Pyrogallol, which has been suggested as a precipitant for antimony[33] and bismuth,[34] gives colour reactions with cerium, thorium, lanthanum, and other elements of the third analytical group.[35] Iron can be separated from beryllium by means of cupferron;[36] details for the microanalytical determination of palladium with dimethylglyoxime, benzoylmethylglyoxime, and salicylaldoxime are given.[37] Glycerol is oxidised in alkaline solution by mercury salts but by no other metals, mercury being quantitatively precipitated.[38] Owing to the formation of complexes with copper, cobalt, nickel, zinc, and cadmium, by addition of glycerol to solutions of these metals, free acid may be directly titrated with sodium hydroxide against methyl-orange.[39]

The colour of mixtures of sulphosalicylic acid and iron solutions is influenced by p_H, phosphate, bivalent manganese, and organic substances; most of these disturbances may be eliminated by the use of citrate buffers and colour filters.[40] The use of picrolonic acid for colorimetric determination of calcium has been reviewed;[41] this reagent has also been applied to the determination of lead.[42] Tin can be separated from many metals by precipitation with phenylarsonic acid,[43] and iron similarly with *p*-*n*-butylphenylarsonic acid; [44] zirconium and thorium, in particular, interfere.

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[29] H. Funk and M. Demmel, *Z. anal. Chem.*, 1934, **96**, 385; *A.*, 621; see *Ann. Reports*, 1933, **30**, 282.

[30] A. Hemmeler, *Ann. Chim. appl.*, 1934, **24**, 140; *A.*, 621; cf. Jakobson, *Metal Ind.*, 1921, **19**, 380.

[31] I. M. Kolthoff, V. A. Stenger, and B. Moskovitz, *J. Amer. Chem. Soc.*, 1934, **56**, 812; *A.*, 621.

[32] L. Lehrman, H. Weisberg, and E. A. Kabat, *ibid.*, p. 1836; *A.*, 1192.

[33] F. Feigl, *Z. anal. Chem.*, 1924, **64**, 41; *A.*, 1924, ii, 571.

[34] F. Feigl and H. Ordelt, *ibid.*, 1925, **65**, 448; *A.*, 1925, ii, 442.

[35] F. M. Schemjakin, *Z. anorg. Chem.*, 1934, **217**, 272; *A.*, 621.

[36] A. Tettamanzi, *Ind. chim.*, 1934, **9**, 752; *A.*, 857.

[37] H. Holzer, *Z. anal. Chem.*, 1933, **95**, 392; *A.*, 1934, 271.

[38] M. Stschigol, *ibid.*, 1934, **96**, 328, 330; *A.*, 621.

[39] H. Wagner, *ibid.*, 1933, **95**, 311; *A.*, 1934, 162.

[40] F. Alten, H. Wieland, and E. Hille, *Z. anorg. Chem.*, 1933, **215**, 81; *A.*, 1934, 49.

[41] F. Alten, H. Wieland, and E. Knippenberg, *Biochem. Z.*, 1933, **265**, 85; *A.*, 1933, 1262.

[42] F. Hecht, W. Reich-Rohrwig, and H. Brantner, *Z. anal. Chem.*, 1933, **95**, 152; *A.*, 1934, 162.

Much work is still being done universally on the determination of sodium as triple uranyl acetate,[45] and on the direct titration of sulphate and barium with rhodizonic acid as indicator.[46]

2-Aminopyridine gives characteristic crystalline compounds with salts of cobalt, copper, zinc, and cadmium and alkali thiocyanate; [47] addition of thiocyanate and *p*-phenylenediamine to neutral or ammoniacal copper solutions produces a black complex compound.[48]

Diphenyl-carbazide and -carbazone can be used as indicators in mercurimetric titrations; [49] dithizone is applied to the detection of zinc, after removal of cadmium, copper, and mercury,[50] and quantitatively for lead and copper.[51]

No entrainment of precipitant or metals occurs in the determination of nitrate with nitron acetate; [52] certain diphenylamine azo-dyes can be used as indicators in the titration of primary amines by sodium nitrite.[53]

The use of organic liquids as adjuncts to analytical manipulation is one which is receiving attention in these times no less than that of organic reagents for precipitations or for colorimetric tests. Some such applications are of long standing as, *e.g.*, the use of ether as a solvent for the extraction of ferric chloride from hydrochloric acid solutions or as an agent to promote agglomeration of silver halide precipitates, of amyl alcohol as a solvent for lithium chloride, of ethyl alcohol in the separation of potassium and sodium as perchlorates. In the last example, it is suggested that the volume of alcohol usually used for washing the perchlorates is insufficient to remove the sodium salt completely; [54] accordingly, the proposal is made to double the volume, using alcohol saturated with potassium perchlorate in order to avoid loss. In the analytical separation of potassium chloroplatinate by means of ethyl alcohol, reduction occurs if the latter contains acetaldehyde; this constitutes a serious source of error in micro-analytical work where the amount of alcohol is relatively large.[55] Potassium iodoplatinate is still more sensitive. The most suitable solvent for the separation of sodium and potassium as iodides is a mixture of equal volumes of *iso*butyl alcohol and ether, both anhydrous.[56] Thallium may be separated from most other metals by extracting with ether in the presence of *N*-hydrobromic acid; [57] a separation from gold, which also passes into the ethereal layer, is then described.

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[43] J. S. Knapper, K. A. Craig, and G. C. Chandlee, *J. Amer. Chem. Soc.*, 1933, **55**, 3945; *A.*, 1933, 1263.

[44] K. A. Craig and G. C. Chandlee, *ibid.*, 1934, **56**, 1278; *A.*, 858.

[45] E. R. Caley, C. T. Brown, and H. P. Price, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 202; *A.*, 745; T. Noda, *J. Soc. Chem. Ind. Japan*, 1933, **36**, 635B; *A.*, 1934, 47; F. Alten, H. Weiland, and E. Hille, *Z. Pflanz. Düng.*, 1933, **32**, [*A*], 129; *A.*, 1934, 47; T. C. Chang and C. L. Tseng, *Sci. Quart. Nat. Univ. Peking*, 1934, **4**, 185; *A.*, 501; I. I. Nazarov and L. P. Banina, *Zavod. Lab.*, 1934, **3**, 226; *A.*, 857; S. Z. Makarov and V. V. Bukina, *J. Gen. Chem. Russia*, 1933, **3**, 881; *A.*, 501.

[46] J. C. Giblin, *Analyst*, 1933, **58**, 752; *A.*, 161; A. Friedrich and S. Rapoport, *Mikrochem.*, 1933, **14**, 41; *A.*, 1933, 1262; R. B. Roschal, *Anilinokras. Prom.*, 1934, **4**, 37; *A.*, 500; M. N. Maruschkin, *J. Appl. Chem. Russia*, 1933, **6**, 951; *A.*, 46; W. C. Schroeder, *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 403; *A.*, 1934, 46.

[47] A. Sá, *Anal. Farm. Bioquim.*, 1933, **4**, 77; *A.*, 1934, 502.

[48] R. J. McIlroy, *Analyst*, 1934, **59**, 103; *A.*, 382.

[49] J. V. Dubský and J. Trtílek, *Chem. Listy*, 1933, **27**, 385; *A.*, 1934, 49; *Mikrochem.*, 1934, **115**, 95; *A.*, 744; J. Trtílek, *Coll. Czech. Chem. Comm.*, 1933, **5**, 302; *A.*, 1933, 1260.

[50] G. Rienäcker and W. Schiff, *Z. anal. Chem.*, 1933, **94**, 409; *A.*, 48.

[51] H. Fischer and (Frl.) G. Leopoldi, *Angew. Chem.*, 1934, **47**, 90; *A.*, 381.

[52] J. E. Heck, H. Hunt, and M. G. Mellon, *Analyst*, 1934, **59**, 18; *A.*, 268.

[53] A. E. Porai-Kochitz and L. V. Tschervinskaja, *Anilinokras. Prom.*, 1933, **3**, 339; *A.*, 1934, 161.

The addition of gum tragacanth or gelatin prevents the turbidity which often occurs in the diethyldithiocarbamate process for minute amounts of copper.[58] As a solvent in this process, *iso*amyl alcohol, redistilled at 129—131°, is preferred to the *n*-alcohol.[59] In the *iso*amyl alcohol modification of the thiocyanate method for small quantities of iron,[60] fading of the coloration has been experienced as well as the introduction of undesirable colours due to calcium salts; [61] the presence of nitric acid in place of other mineral acid assists in correcting both of these features. *iso*Propyl alcohol may be used in place of ethyl alcohol as a solvent for analytical reagents, as a washing medium for precipitates, and for the separation of inorganic compounds.[62]

Ammonium salts give with sodium hypobromite and phenols an intense blue coloration, turning red on acidification;[63] that from thymol may be extracted with organic solvents, *e.g.*, ether. Other cations and organic bases (other than aniline) do not interfere.

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[54] M. Lenglen and Milhiet, *Ann. Falsif.*, 1933, **26**, 469; *A.*, 1933, 1262.

[55] R. Strebinger and H. Holzer, *Z. anal. Chem.*, 1932, **90**, 81; *A.*, 1932, 1222.

[56] L. Szebellédy and K. Schick, *Magyar Gyóg. Társas. Ért.*, 1933, **9**, 40; *A.*, 161.

[57] I. Wada and R. Ishü, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **24**, 135; *Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 20; *A.*, 857.

[58] H. W. Moseley, A. G. Rohwer, and M. C. Moore, *Science*, 1934, **79**, 507; *A.*, 858.

[59] R. W. Thatcher, *J. Amer. Chem. Soc.*, 1933, **55**, 4524; *A.*, 1934, 49.

[60] R. Stugart, *Ind. Eng. Chem. (Anal.)*, 1931, **3**, 390; *B.*, 1932, 78.

[61] H. A. Daniel and H. J. Harper, *J. Assoc. Off. Agric. Chem.*, 1934, **17**, 286; *A.*, 858.

[62] G. W. Ferner and M. G. Mellon, *Ind. Eng. Chem. (Anal.)*, 1934, **6**, 345; *A.*, 1193; cf. F. M. Archibald and C. M. Beamer, *ibid.*, 1932, **4**, 18; *B.*, 1932, 250.

In qualitative tests involving the formation of insoluble compounds, sensitivity may frequently be increased by the addition of an immiscible liquid, causing the precipitate to collect at the interface.[64]

Crystalline character and high molecular weight are features of many precipitates obtained by organic reagents from solutions of inorganic substances. The analytical application of wholly inorganic compounds possessing these desirable properties is, therefore, not without interest. The reagent is a 10% aqueous solution of potassium mercuri-iodide which, when used for nickel or cadmium, should contain excess of potassium iodide. The precipitate from copper, in ammoniacal solution and in presence of ammonium nitrate, has the composition $[Cu(NH_3)_4][HgI_3]_2$ and contains 4·91% of copper. The precipitates, though decomposed by water alone, may be prepared for weighing by washing with alcohol, saturated with the appropriate compound, then with ether, and dried in a vacuum. Nickel may be separated from cobalt after oxidising the latter with hydrogen peroxide in the ammoniacal solution.[65]

Mercurous iodate is sufficiently insoluble to be utilised analytically for mercury either gravimetrically or volumetrically;[66] the reaction may also be followed potentiometrically.[67] Qualitative tests have been described for iodate and periodate in the presence of each other.[68]

Coagulation, filtration, and washing of barium sulphate are rapid when co-precipitation with aluminium hydroxide is effected.[69]

Organic Compounds.—The following reagents have been investigated for the purpose of identifying aldehydes and ketones: *o*-tolylhydrazine,[70] *p*-tolyl- and *p*-chlorophenyl-hydrazine,[71] β-naphthylhydrazine,[72] phenylsemicarbazide,[73] *p*-tolylsemicarbazide,[74]

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[63] L. Lapin and W. Hein, *Z. anal. Chem.*, 1934, **98**, 236; *A.*, 1189.

[64] *E.g.*, F. Feigl and H. Ordelt, *ibid.*, 1925, **65**, 448; *A.*, 1925, ii, 442; Feigl *et al.*, *Mikrochem.*, 1931, **9**, 165; *A.*, 1931, 590.

[65] A. Tauriņš, *Z. anal. Chem.*, 1934, **97**, 27; *A.*, 620.

[66] G. Spacu and P. Spacu, *ibid.*, **96**, 30; *A.*, 270.

[67] *Idem, ibid.*, p. 188; *A.*, 502.

[68] H. H. Willard and J. J. Thompson, *J. Amer. Chem. Soc.*, 1934, **56**, 1827; *A.*, 1189.

[69] J. E. Orlov, *Z. anal. Chem.*, 1934, **98**, 326; *A.*, 1189.

[70] P. P. T. Sah and T. S. Ma, *Sci. Rep. Nat. Tsing Hua Univ.*, 1932, [*A*], **1**, 259; *A.*, 1933, 498.

[71] P. P. T. Sah, H. H. Lei, and T. Shen, *ibid.*, **2**, 1, 7; *A.*, 1933, 964.

[72] H. H. Lei, P. P. T. Sah, and C. H. Kao, *ibid.*, p. 335; *A.*, 1376.

[73] P. P. T. Sah and T. S. Ma, *J. Chinese Chem. Soc.*, 1934, **2**, 32; *A.*, 791.

[74] P. P. T. Sah and H. H. Lei, *ibid.*, p. 167; *A.*, 1016.

3 : 5-dinitrobenzoylhydrazine,[75] 3-nitro-,[76] *o*-chloro-,[77] and *p*-chlorobenzoylhydrazine,[78] nitrobenzenesulphonhydrazine.[79] 2 : 4-Dinitrophenylhydrazones of ketonic acids of biological importance have been characterised; [80] in view of the presence of traces of aldehydes in ethyl alcohol, 2 : 4-dinitrophenylhydrazine is best used in methyl-alcoholic solution.[81] 1 : 3-Dimethylbarbituric acid reacts rapidly with furfuraldehydes and aromatic aldehydes.[82]

Phenacyl and *p*-bromophenacyl esters of dibasic acids [83] and of monosubstituted benzoic acids [84] are described, also aryl *p*-bromobenzenesulphonates from phenols and the acid chloride in pyridine.[85] Some β-naphthyl ethers form picrates; [86] the use of styphnic acid as a reagent for the identification of aromatic compounds containing benzene nuclei,[87] of heterocyclic nitrogen compounds, and of alkaloids [88] is recorded.

3-Nitro-[89] and tetrachloro-phthalimide [90] react, as the potassio-derivatives, to give crystalline *N*-substituted derivatives with organic halogen compounds: alkyl chlorides are readily converted into substituted amides *via* the alkylmagnesium compounds; the *p*-toluidides are useful for distinguishing between chlorides of similar boiling point.[91] The list of sulphides obtained from mercaptans by reaction with 1-chloro-2 : 4-dinitrobenzene has been extended.[92] Reactions of amines have been examined with α-naphthylthiocarbimide,[93] ethyl sulphonediacetate,[94] *m*-nitrophenylthiocarbimide,[95] 3 : 5-dinitrobenzazide,[96] nitrocarbamide,[97] 2 : 4-dinitrobenzoyl chloride,[98] and, for amino-acids, 3 : 5-dinitrobenzoyl chloride.[99]

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[75] P. P. T. Sah and T. S. Ma, *J. Chinese Chem. Soc.*, 1934, **2**, 40; *A.*, 790.

[76] K. C. Meng and P. P. T. Sah, *ibid.*, p. 347; *A.*, 1376.

[77] T. H. Sun and P. P. T. Sah, *ibid.*, p. 359; *A.*, 1376.

[78] C. Shih and P. P. T. Sah, *ibid.*, p. 353; *A.*, 1376.

[79] J. M. L. Cameron and F. R. Storrie, *J.*, 1934, 1330.

[80] F. P. Clift and R. P. Cook, *Biochem. J.*, 1932, **26**, 1800; *A.*, 1933, 489.

[81] J. Ferrante and A. Bloom, *Amer. J. Pharm.*, 1933, **105**, 381; *A.*, 1933, 1053.

[82] S. Akabori, *Ber.*, 1933, **66**, [*B*], 139; *A.*, 1933, 284.

[83] T. L. Kelly and P. A. Kleff, *J. Amer. Chem. Soc.*, 1932, **54**, 4444; *A.*, 1933, 52.

[84] T. L. Kelly and H. W. Howard, *ibid.*, p. 4383; *A.*, 1933, 64.

[85] V. C. Sekera, *ibid.*, 1933, **55**, 421; *A.*, 1933, 270.

[86] A. B. Wang, *J. Chinese Chem. Soc.*, 1933, **1**, 59; *A.*, 1933, 1157.

[87] T. S. Ma, C. T. Hsia, and P. P. T. Sah, *Sci. Rep. Nat. Tsing Hua Univ.*, 1933, **2**, 151; *A.*, 1934, 540.

[88] V. Hoo, T. S. Ma, and P. P. T. Sah, *ibid.*, pp. 191, 245; *A.*, 1934, 540, 1017.

[89] P. P. T. Sah and T. S. Ma, *Ber.*, 1932, **65**, [*B*], 1630; *A.*, 1932, 1231.

[90] C. G. F. Allen and R. V. V. Nicholls, *J. Amer. Chem. Soc.*, 1934, **56**, 1409; *A.*, 910.

[91] H. W. Underwood, jun., and J. C. Gale, *ibid.*, p. 2117; *A.*, 1330.

[92] R. W. Bost, J. O. Turner, and M. W. Conn, *ibid.*, 1933, **55**, 4956; *A.*, 1934, 170.

Data are given for various amides of hexoic acids [1] and numerous esters of 1-nitroanthraquinone-2-carboxylic acid; [2] the melting points of some compounds of aldehydes with methone are revised and the list extended.[3]

In many of the above cases, improvements have been made in the preparation of the reagents.

The presence of bisulphite assists in the crystallisation of osazones and hydrazones of sugars.[4]

The term " aminometry " is applied to the volumetric determination of amines by acids with exclusion as completely as possible of aqueous and alcoholic solvents and of all conditions under which amines become bases; [5] cinchonine and quinine behave quantitatively as diacid amines, whereas strychnine and brucine are monoacid.[6] Salts of the last two yield precipitates with potassium dichromate which can be dried to definite hydrates over deliquescent sodium bromide; [7] strychnine, and brucine less satisfactorily, can be precipitated and weighed as hydroferrocyanide.[8] Hexamethylenetetramine can be determined by precipitation of its uranyl double sulphate [9] and argentometrically following precipitation with excess of silver nitrate.[10]

In the bromometric determination of furfural, temperature is very important, since the secondary reaction (formation of tetrabromide) has a high temperature coefficient.[11] Furfural can be determined by precipitation with barbituric acid without interference from hydroxymethylfurfural, which is not precipitated at the concentrations encountered in the analysis of pentosans.[12]

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[93] C. M. Suter and E. W. Moffett, *J. Amer. Chem. Soc.*, 1934, **56**, 2497; *A.*, 1933, 816.

[94] J. P. Alden and B. Houston, *ibid.*, 1934, **56**, 413; *A.*, 396.

[95] P. P. T. Sah and H. H. Lei, *J. Chinese Chem. Soc.*, 1934, **2**, 153; *A.*, 997.

[96] P. P. T. Sah and T. S. Ma, *ibid.*, p. 159; *A.*, 997.

[97] P. P. T. Sah, *Sci. Rep. Nat. Tsing Hua Univ.*, 1934, **2**, 227; *A.*, 997.

[98] C. A. Buehler and J. D. Calfee, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 351; *A.*, 1240.

[99] B. C. Saunders, *Biochem. J.*, 1934, **28**, 580; *A.*, 638.

[1] M. Hommelen, *Bull. Soc. chim. Belg.*, 1933, **42**, 243; *A.*, 1933, 933.

[2] P. P. T. Sah and T. S. Ma, *J. Chinese Chem. Soc.*, 1933, **1**, 51; *A.*, 1933, 1033.

[3] C. H. Kao and J. Y. Yen, *Sci. Rep Nat. Tsing Hua Univ.*, 1932, **1**, 185; *A.*, 1932, 1235.

[4] M. Wagenaar, *Pharm. Weekblad*, 1934, **71**, 229; *A.*, 394; R. H. Hamilton, jun., *J. Amer. Chem. Soc.*, 1934, **56**, 487; *A.*, 394.

[5] D. Vorländer, J. Fischer, and F. Wildner, *Ber.*, 1933, **66**, [*B*], 1789; *A.*, 1934, 198.

[6] D. Vorländer, *ibid.*, 1934, **67**, [*B*], 145; *A.*, 314.

[7] I. M. Kolthoff and J. J. Lingane, *J. Amer. Pharm. Assoc.*, 1934, **23**, 404; *A.*, 911.

[8] *Idem, ibid.*, p. 302; *A.*, 672.

[9] Foucry, *J. Pharm. Chim.*, 1934, [viii], **20**, 168; *A.*, 1093.

[10] J. von Mikó, *Pharm. Zentr.*, 1933, **74**, 642; *A.*, 1934, 175.

Picric acid is quantitatively precipitated by ammoniacal solutions of copper sulphate; the reaction can be applied gravimetrically or volumetrically.[13]

B. A. E.

3. Oxidation–Reduction Indicators.

Although certain dyes, particularly methylene-blue, had been used in volumetric work and in biological studies to indicate the presence of a reducing agent, much as litmus was at one time used to show the presence of acid, in recent years the study of oxidation–reduction indicators has developed to an extent parallel to that of acid–base indicators. The applications of the former, like those of the latter, fall into two categories: (*a*) in the determination of oxidation–reduction potentials, and (*b*) in the indication of end-points in oxidation–reduction titrations.

Oxidation–Reduction Potentials.—The oxidation–reduction intensity of a *thermodynamically reversible* system containing an oxidised and a reduced form is determined by the potential acquired by an unattackable electrode when inserted in the solution under consideration; for the process represented by

$$a\mathrm{A} + b\mathrm{B} + \ldots + n\ominus \rightleftharpoons x\mathrm{X} + y\mathrm{Y} + \ldots$$

the electrode potential E is given by the expression

$$E = E_0 + RT/nF \,.\, \log_e (a_\mathrm{A}^a \,.\, a_\mathrm{B}^b \ldots)/(a_\mathrm{X}^x \,.\, a_\mathrm{Y}^y \ldots)$$

where E_0 is the "standard oxidation–reduction potential" of the system, and the a terms represent the corresponding activities of ions or molecules. If neither oxidant nor reductant involves hydrogen ions, the electrode potential will be independent of the acidity of the solution, but will be determined by the ratio of the activities (or concentrations) of the oxidised and reduced forms; this is the case with the ferric–ferrous system, provided complex-forming organic ions, the concentrations of which are influenced by the p_H, are absent.[1] Many systems, especially those of biological interest and those concerned with oxidation–reduction indicators, involve at some stage a thermodynamically reversible process in which hydrogen ions are concerned, and so the potentials in these cases depend on the p_H of the solution. In the simplest case, the oxidation–reduction equilibrium may be written: $Q + 2H^{\cdot} + 2\ominus \rightleftharpoons H_2Q$, and the electrode potential on the hydrogen scale is given by

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[11] E. E. Hughes and S. F. Acree, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 123; *A.*, 540; see also T. S. Krishnan, *J. Indian Chem. Soc.*, 1934, **11**, 651; *A.*, 1337.

[12] B. Peter, H. Thaler, and K. Täufel, *Z. Unters. Lebensm.*, 1933, **66**, 143; *A.*, 1933, 1278.

[13] A. Zacharov, *J. Appl. Chem. Russia*, 1933, **6**, 998; *A.*, 1934, 90.

[1] P. Hirsch and R. Rüter, *Z. anal. Chem.*, 1926, **69**, 193; *A.*, 1927, 23; L. Michaelis and E. Friedheim, *J. Biol. Chem.*, 1931, **19**, 343; *A.*, 1931, 687.

$$E_h = E_0 + RT/2F \,.\, \log_e [Q]/[H_2Q] + RT/F \,.\, \log_e [H^{\cdot}],$$

concentrations being used instead of activities for simplicity. The potential of a hydrogen electrode with gas at 1 atm. pressure in the same solution will be $RT/F \,.\, \log_e [H^{\cdot}]$, and thus the *E.M.F.* of a hypothetical cell consisting of such an electrode and the given oxidation–reduction electrode should remain constant independently of changes in the p_H of the medium. It is evident, therefore, that the latter electrode must be equivalent to a hydrogen electrode operating at a pressure P, determined by the relationship

$$E_h = RT/2F \,.\, \log_e 1/P + RT/F \,.\, \log_e [H^{\cdot}].$$

The hypothetical pressure P, and consequently a term r_H, defined as $-\log P$, should thus be a measure of the oxidation intensity of the system independent of the p_H of the medium.[2] The higher the r_H value of a given system, the higher its oxidation–reduction intensity.

So far, it has been assumed that neither the oxidised nor the reduced form has acidic or basic functions, but as the former is often a quinone or a quinone-imine, the latter, at least, must contain hydroxyl- or amino-groups; the electrode-potential equation under these conditions will include the various acidic and basic dissociation constants of both oxidised and reduced states.[3] The r_H for such a system is no longer independent of the p_H of the medium, and it does not adequately define the oxidation intensity. The use of r_H is thus liable to lead to confusion, and for this reason it should be used with caution.[4] In spite of its limitations, the r_H is often convenient for the description of biological systems: the p_H of these is generally in the vicinity of 7, and if the r_H is stated for this value it can be regarded as remaining constant within the narrow limits of p_H variation likely to be encountered.[5]

Oxidation–Reduction Indicators.—An oxidation–reduction indicator is, in general, a substance which in the oxidised state has a quinonoid structure and an intense colour; on reduction it takes up two atoms of hydrogen per molecule, as in the simple example already considered, forming a feebly-coloured leuco-compound. If a small quantity of such a substance, which must attain equilibrium rapidly, is added to a relatively large amount of solution containing an oxidation–reduction system to be examined, the indicator is either oxidised or reduced until its own potential, *at the* p_H *of the medium*, is the same as that of the given system. The depth of colour shown by the indicator, which is determined by the relative amounts of oxidised and reduced forms, will thus vary with the oxidation–reduction potential of the solution being tested. If E_0' is the potential of the indicator system containing equimolar amounts of these two forms, at the p_H of the medium, then the indicator will show an intermediate colour when placed in a solution having the same potential. Small variations of potential on either side of E_0' will become evident by corresponding changes in the depth of the indicator colour. An appropriate oxidation–reduction indicator can thus be used to determine colorimetrically the potential of a given solution, but as the indicators are generally of the one-colour type, the results are only approximate.[6] If one indicator is decolorised by the solution and another not, then the E_h of the system lies between the E_0' values for the two indicators at the p_H of the solution.[7] Oxidation–reduction indicators are also used as " potential mediators " in biological media for which electrode equilibrium is only attained slowly; the potential is then measured electrometrically. When employing indicators for any purpose it is essential that the solution to which it is added should be well " poised," [8] *i.e.*, buffered in the oxidation–reduction sense, so that in oxidising or reducing the indicator the ratio of oxidised to reduced states in the system under examination is not appreciably altered.

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[2] W. M. Clark and B. Cohen, *U.S. Pub. Health Rep.*, 1923, No. 826.

[3] *Idem, ibid.*

[4] W. M. Clark, *U.S. Hyg. Lab. Bull.*, 1928, No. 151, Suppl. notes, p. 342; "The Determination of Hydrogen Ions," 1928.

[5] L. Michaelis, "Oxydations-Reductions Potentiale," 1933.

In order to determine the effective range of an indicator, a known amount of the completely oxidised, or of the completely reduced, form is titrated electrometrically, using an inert electrode, with a standard solution of a powerful reducing, or oxidising, agent respectively, in a series of buffer solutions of known p_H; from the measured potentials, the value of E_0' at each p_H is determined.[9] In some cases the results are extrapolated to p_H 0 to give the standard oxidation–reduction potential E_0 of the indicator system. An alternative method of determining E_0', which appears to be of limited applicability, depends on the use of "poised solutions," made up from ferric and ferrous salts in the presence of oxalates, and from cupric and cuprous salts in potassium chloride solutions.[10] The effective range of an indicator is often stated in terms of r_H calculated from its E_0' potential at p_H 7; although, as already shown, this is not a fundamental constant, it provides an approximate standard of comparison for biological work. The indicator will be oxidised by a system having a higher r_H, and reduced by one with a lower value.

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[6] H. D. Gibbs, B. Cohen, and R. K. Cannan, *U.S. Pub. Health Rep.*, 1925, No. 1001; *A.*, 1926, 60.

[7] See, *e.g.*, J. Needham and (Mrs.) D. M. Needham, *Proc. Roy. Soc.*, 1925, [*B*], **98**, 259; *A.*, 1925, i, 1012; *idem, ibid.*, 1926, [*B*], **99**, 173, 383; *A.*, 1926, 194, 545; B. Cohen, R. Chambers, and P. Reznikoff, *J. Gen. Physiol.*, 1928, **11**, 585; *A.*, 1928, 793; R. Chambers, B. Cohen, and H. Pollack, *Brit. J. Exp. Biol.*, 1929, **6**, 229.

[8] W. M. Clark, *U.S. Pub. Health Rep.*, 1923, No. 823; *A.*, 1923, ii, 677; M. Phillips, W. M. Clark, and B. Cohen, *ibid.*, 1927, Suppl. No. 61; *A.*, 1928,

The majority of substances proposed as oxidation–reduction indicators are also acid–base indicators, being frequently blue in alkaline solution and reddish-brown in acid. The latter colour is much less intense than the former, and so it is desirable to use the indicator in the blue form. In biological work it is often not permissible to alter the p_H from the vicinity of 7, and hence indicators are required with relatively strongly acidic or weakly basic groups, so that they show their alkaline colours at relatively low p_H values. This has been achieved in the phenol–indophenol series by introducing halogen atoms into one of the phenolic residues.[11] More than 70 coloured substances have been studied from the oxidation–reduction standpoint,[12] but on account of their instability, sensitivity to light, sparing solubility, or other disadvantages, only a limited number are suitable for use as indicators. The following have been recommended: indigo-disulphonate, -trisulphonate, and -tetrasulphonate, methylene-blue, toluylene-blue, 1-naphthol-2-sulphonate indo-2 : 6-dichlorophenol, 1-naphthol-2-sulphonate indophenol, 2 : 6-dichlorophenol indo-*o*-cresol, *m*-toluylenediamine indophenol, 2 : 6-dichlorophenol indophenol, *o*-chlorophenol indophenol, phenol-*o*-sulphonate indo-2 : 6-dibromoindophenol, *m*-chlorophenol indo-2 : 6-dichloroindophenol, and phenol-*m*-sulphonate indo-2 : 6-dibromophenol.[13] The range of E_0' values covered at p_H 7·0 is from $-$ 0·125 to $+$ 0·273 volt at 30°, *i.e.*, r_H 10 to 23. For solutions with more negative potentials the indicators available, mostly pheno- and apo-safranines,[14] are not very satisfactory, but it is possible that the recently discovered "viologens," which are *NN'*-disubstituted-4 : 4'-dipyridylium chlorides,[15] may prove of considerable value. These substances are remarkable in being coloured in the reduced state, the E_0' potentials being as low as $-$ 0·4 volt at p_H 7.

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[9] Cf. W. M. Clark and B. Cohen, *U.S. Pub. Health Rep.*, 1923, No. 834; *A.*, 1923, ii, 726; M. X. Sullivan, B. Cohen, and W. M. Clark, *ibid.*, 1923, No. 848; *A.*, 1924, i, 321.

[10] P. Hirsch and R. Rüter, *loc. cit.*

[11] B. Cohen, H. D. Gibbs, and W. M. Clark, *U.S. Pub. Health Rep.*, 1924, Nos. 904 and 915; *A.*, 1924, ii, 597; 1925, i, 25; H. D. Gibbs, B. Cohen, and R. K. Cannan, *loc. cit.*

[12] W. M. Clark and B. Cohen, *loc. cit.*; M. X. Sullivan, B. Cohen, and W. M. Clark, *loc. cit.*; B. Cohen, H. D. Gibbs, and W. M. Clark, *locc. cit.*; H. D. Gibbs, B. Cohen, and R. K. Cannan, *loc. cit.*; W. M. Clark, B. Cohen, and H. D. Gibbs, *ibid.*, 1925, No. 1017; 1926, Suppl. No. 54; *A.*, 1925, ii, 1164; 1926, 1008; M. Phillips, W. M. Clark, and B. Cohen, *loc. cit.*; H. D. Gibbs, W. L. Hall, and W. M. Clark, *ibid.*, 1928, Suppl. No. 69; *A.*, 1929, 816; W. L. Hall, P. W. Preisler, and B. Cohen, *ibid.*, 1928, Suppl. No. 71; *A.*, 1929, 769; B. Cohen and M. Phillips, *ibid.*, 1929, Suppl. No. 74; *A.*, 1930, 165; B. Cohen and P. W. Preisler, *ibid.*, 1931, Suppl. No. 92; *A.*, 1931, 1013; W. M. Clark and M. E. Perkins, *J. Amer. Chem. Soc.*, 1932, **54**, 1228; *A.*, 1932, 472; R. D. Stiehler, T. T. Chen, and W. M. Clark, *ibid.*, 1933, **55**, 891; *A.*, 1933, 464; R. D. Stiehler and W. M. Clark, *ibid.*, 1933, **55**, 4097; *A.*, 1933, 1248; E. Vellinger, *Arch. Phys. biol.*, 1929, **7**, 113; L. Rapkine, A. P. Struyk, and R. Wurmser, *J. Chim. physique*, 1929, **26**, 340; *A.*, 1929, 1147; L. Michaelis, *J. Biol. Chem.*, 1931, **91**, 369; *A.*, 1931, 687; *ibid.*, 1931, **92**, 211; *A.*, 1931, 1309; *J. Amer.*

Indicators in Volumetric Analysis.—When an oxidising agent is coloured, it can often act as its own indicator in volumetric analysis: this is the case with permanganate and to some extent with iodine. Methylene-blue has been frequently used as a reagent in the titration of titanous chloride, and a recent development of the same type is the employment of 2 : 6-dichloro- (or -dibromo-)phenol indophenol as titrant for the estimation of vitamin-*C*.[16] In other instances,

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Chem. Soc., 1931, **53**, 2953; *A.*, 1931, 1129; *Biochem. Z.*, 1932, **250**, 564; *A.*, 1932, 1102; L. Michaelis and H. Eagle, *J. Biol. Chem.*, 1930, **87**, 713; *A.*, 1930, 1142; E. Friedheim and L. Michaelis, *ibid.*, 1931, **91**, 355; *A.*, 1931, 684; L. Michaelis, E. S. Hill, and M. P. Schubert, *Biochem. Z.*, 1932, **255**, 66; *A.*, 1933, 97; L. Michaelis and E. S. Hill, *J. Gen. Physiol.*, 1933, **16**, 589; *A.*, 1933, 958; *J. Amer. Chem. Soc.*, 1933, **55**, 1481; *A.*, 1933, 611; B. Elema, *Rec. trav. chim.*, 1931, **50**, 807; *A.*, 1931, 1013; *ibid.*, 1933, **52**, 569; *A.*, 1933, 909; M. Letort, *Compt. rend.*, 1932, **194**, 711; *A.*, 1932, 343; E. Friedheim, *Biochem. Z.*, 1933, **259**, 257; *A.*, 1933, 622; K. G. Stern, *Biochem. J.*, 1934, **28**, 949; *A.*, 846; R. Kuhn and T. Wagner-Jauregg, *Ber.*, 1934, **67**, [*B*], 361; *A.*, 461; see also K. G. Stern, *ibid.*, p. 654; *A.*, 817.

[13] W. L. Hall, P. W Preisler, and B. Cohen, *loc. cit.*; B. Cohen and M. Phillips, *loc. cit.*

[14] R. D. Stiehler, T. T. Chen, and W. M. Clark, *loc. cit.*; R. D. Stiehler and W. M. Clark, *loc. cit.*

[15] L. Michaelis, *Biochem. Z.*, 1932, **250**, 564; *A.*, 1932, 1102; L. Michaelis and E. S. Hill, *locc. cit.*

[16] Cf. J. Tillmans, P. Hirsch, and R. Vaubel, *Z. Unters. Lebensm.*, 1933, **65**, 145; *A.*, 1933, 433; J. W. Birch, L. J. Harris, and S. N. Ray, *Biochem. J.*, 1933, **27**, 590; *A.*, 1933, 646; J. L. Svirbely, *ibid.*, p. 960; *A.*, 1933, 872; A. H. Bennett, *Analyst*, 1934, **59**, 91; *A.*, 462.

e.g., dichromate and ceric sulphate, external indicators or potentiometric methods had to be applied for the determination of end-points. The application of the familiar fact that diphenylamine can be oxidised to a violet-blue compound to indicate the equivalence point in the titration of ferrous iron by dichromate,[17] has stimulated interest in the development of internal oxidation–reduction indicators for use in volumetric analysis. The indicators already discussed are of little value in this connexion, because (*a*) their colour-change potentials are too low, (*b*) the colours are relatively feeble in acid solutions, and (*c*) they are relatively unstable.

The indicator action of diphenylamine is to be ascribed to a primary irreversible oxidation to diphenylbenzidine, followed by reversible oxidation of the latter, which is colourless, to diphenylamine-violet, with a green meriquinone as intermediate; the holoquinone has an intense violet colour in solutions of low acidity and is blue in solutions which are more than $4N$ with respect to strong acid. The marked colour change from green to violet occurs at about 0·76 volt (on the hydrogen scale) independently of the acidity of the solution. The rate at which the violet colour develops in the presence of dichromate increases with the acidity, as does the oxidation potential, but with permanganate, which has a more positive potential, the colour develops instantaneously at any reasonable acidity.[18] It was at one time thought that the colour development required the presence of ferrous ions,[19] but this is not the case [20] although these ions increase enormously the rate at which the violet colour appears. In the titration of ferrous ions by dichromate in acid solution the end-point is sharp provided phosphoric acid or a fluoride is added; [21] these substances form complexes with the ferric ions and so reduce the potential of the ferric–ferrous system below that at which the diphenylbenzidine colour change occurs. When diphenylamine is employed as indicator it is necessary to apply a correction, equivalent to the quantity of indicator present, because of the oxidant used up in converting it into diphenylbenzidine; [22] this correction can be avoided by adding the latter itself as indicator,[23] but owing to its sparing solubility this is rarely done. Diphenylbenzidine-violet suffers irreversible oxidation, forming an insoluble compound and leaving a colourless solution to which the violet colour cannot be restored;[24] consequently, if the indicator is to be used for back titrations the time of contact with the oxidising solution should be kept at a minimum. Although it was first considered that diphenylamine could be used in the presence of mercuric ions,[25] it has been shown that they inhibit the formation of the violet colour,[26] and even traces of tungstate ions exert a similar effect.[27] Many of the disadvantages of diphenylamine itself can be avoided by the employment of the sulphonic acid, as its barium salt. This is readily soluble in acid solutions and it changes colour at a potential of about 0·83 volt, in a manner similar to that of diphenylamine. The presence of ferrous ions accelerates the normally slow transition from green to violet, and a sharply reversible brilliant colour change occurs at the end-point in the ferrous–dichromate titration which is not masked even in coloured solutions. Mercuric ions and tungstate ions have no influence on the development of the violet colour under these conditions.[28] The correction for the oxidation of the indicator is larger than would be expected theoretically, but the difference is not serious if only a small amount of indicator is used.[29] In addition to the ferrous–dichromate titration, diphenylamine (or its sulphonic acid) has been employed in the following titrations: ferrous ions by permanganate,[30] by vanadate,[31] and by ceric sulphate;[32] chromic acid by titanous sulphate; ferricyanide ions by stannous chloride; uranous ions, cuprous ions in hydrochloric acid, iron–chromium mixtures,[33] and ferrocyanide ions[34] by dichromate; zinc ions by ferrocyanide[35] containing a trace of ferricyanide; and quinol by ceric sulphate and by dichromate.[36]

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[17] J. Knop, *J. Amer. Chem. Soc.*, 1924, **46**, 263; *A.*, 1924, ii, 351.

[18] I. M. Kolthoff and L. A. Sarver, *ibid.*, 1930, **52**, 4179; *A.*, 1931, 54.

[19] J. Knop, *loc. cit.*

[20] W. H. Cone and L. C. Cady, *ibid.*, 1927, **49**, 2214; *A.*, 1927, 1046.

[21] J. Knop, *loc. cit.*; L. A. Sarver, *ibid.*, 1927, **49**, 1472; *B.*, 1927, 557; L. Szebellédy, *Z. anal. Chem.*, 1930, **81**, 97; *A.*, 1930, 1149; C. J. Schollenberger, *J. Amer. Chem. Soc.*, 1931, **53**, 88; *A.*, 1931, 328.

[22] N. H. Furman, *Ind. Eng. Chem.*, 1925, **17**, 314; *A.*, 1925, ii, 442; N. H. Furman and J. H. Wallace, *J. Amer. Chem. Soc.*, 1930, **52**, 1443; *A.*, 1930, 727; L. A. Sarver and I. M. Kolthoff, *ibid.*, 1931, **53**, 2906; *A.*, 1931, 1141.

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[23] W. H. Cone and L. C. Cady, *J. Amer. Chem. Soc.*, 1927, **49**, 356; *A.*, 1927, 331; I. M. Kolthoff, *Chem. Weekblad*, 1927, **24**, 203; *A.*, 1927, 535; H. H. Willard and (Miss) P. Young, *J. Amer. Chem. Soc.*, 1928, **50**, 1334; *A.*, 1928, 725; I. M. Kolthoff and L. A. Sarver, *ibid.*, 1930, **52**, 4179; *A.*, 1931, 54; I. M. Kolthoff and E. A. Pearson, *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 147; *A.*, 1932, 243.

[24] I. M. Kolthoff and L. A. Sarver, *loc. cit.*

[25] J. Knop, *loc. cit.*; W. W. Scott, *J. Amer. Chem. Soc.*, 1924, **46**, 1396; *A.*, 1924, ii, 787.

[26] F. J. Watson, *Chem. Eng. Min. Rev.*, 1928, **20**, 355; I. M. Kolthoff and L. A. Sarver, *loc. cit.*

[27] H. H. Willard and P. Young, *Ind. Eng. Chem.*, 1928, **20**, 769; *B.*, 1928, 643.

[28] L. A. Sarver and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1931, **53**, 2902; *A.*, 1931, 1141.

[29] *Idem, ibid.*, p. 2906; *A.*, 1931, 1141.

[30] W. W. Scott, *loc. cit.*

[31] N. H. Furman, *loc. cit.*; H. H. Willard and P. Young, *ibid.*, 1928, **50**, 1334; *A.*, 1928, 725; *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 154, 158; *B.*, 1933, 550; L. A. Sarver and I. M. Kolthoff, *ibid.*, 1931, **53**, 2906; *A.*, 1931, 1141; K. Someya, *Z. anorg. Chem.*, 1924, **139**, 237; *A.*, 1925, ii, 161; see, however, *idem, ibid.*, 1926, **152**, 391; *A.*, 1926, 705.

A general study has been made of a number of diphenylamine derivatives, of which the most interesting are the *p*-nitro-, *p*-amino-, and 2 : 4-diamino-compounds. The last changes colour from green to violet at about 0·66 volt, and the violet holoquinone is relatively stable to further oxidation;[37] this substance may therefore find application for back titrations. Other substances analogous to diphenylamine in their oxidation–reduction properties[38] have also been used as indicators; *p*-anisidine, *p*-phenetidine, and di-*o*-anisidine, of which the last is the best, have been employed in the titration of ferrous ions by dichromate;[39] benzidine[40] and benzidine acetate[41] for ferrocyanide titration by dichromate; *p*-phenetidine for dichromate against ferrous ions;[42] and *pp*′-diaminodiphenylamine[43] for barium chloride and dichromate.

The following triphenylmethane dyes have been recommended for use in titrations with permanganate, their oxidation potentials being too high for employment with dichromate: acronol brilliant blue BDC, cyanine B, cyano bright green 2G, erio-glaucin A, erio-green B, patent blue A, setocyanine supra, setoglaucin O, setopalin conc., xylene blue AS, xylene blue VS, and xylene cyanol FF. These substances are apparently first oxidised irreversibly to compounds of unknown constitution which act as truly reversible indicators: the colour change on oxidation is from yellow or green to pink, in the presence of acid, and is so marked that titrations may be made in highly coloured solutions. The indicators recommended may be used for titration with permanganate of solutions containing hydrochloric acid provided manganous sulphate is added, and their sensitivity is not affected by mercury salts. The addition of phosphoric acid in the titration of ferrous salts is unnecessary. The correction to be applied for the oxidation of the indicator (0·5—1 c.c. of a 0·1% solution) is negligible when 0·1*N*-permanganate is the titrant.[44] All of the dyes mentioned, except acronol brilliant blue BDC and setoglaucin O, can be used for the microtitration of ferrous ions by permanganate.[45] Erio-glaucin A and erio-green B have also been applied in the titration of ferrocyanides by permanganate,[46] and both of these as well as cyanol blue FF have been recommended as indicators for use with ceric sulphate.[47] The results are satisfactory either in hydrochloric or sulphuric acid solutions, and mercury and tin salts do not interfere with the sensitivity of the indicators.

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[32] H. H. Willard and P. Young, *loc. cit.*; see also N. H. Furman and J. H. Wallace, *J. Amer. Chem. Soc.*, 1930, **52**, 2347; *A.*, 1930, 1012.

[33] K. Someya, *Z. anorg. Chem.*, 1926, **152**, 368, 382, 386; 1927, **160**, 355, 404; 1927, **163**, 206; *A.*, 1926, 702, 705; 1927, 332, 333, 746.

[34] A. J. Berry, *Analyst*, 1929, **54**, 461; *A.*, 1929, 1159.

[35] W. H. Cone and L. C. Cady, *loc. cit.*; I. M. Kolthoff, *Chem. Weekblad*, 1927, **24**, 203; 1929, **26**, 298; *A.*, 1927, 535; 1929, 785.

[36] *Idem*, *Rec. trav. chim.*, 1926, **45**, 745; *A.*, 1926, 1266; N. H. Furman and J. H. Wallace, *J. Amer. Chem. Soc.*, 1930, **52**, 1443; *A.*, 1930, 727.

[37] L. P. Hammett, G. H. Walden, and S. M. Edmonds, *ibid.*, 1934, **56**, 1092; *A.*, 744.

[38] W. M. Clark, B. Cohen, and H. D. Gibbs, *U.S. Pub. Health Rep.*, 1926, Suppl. No. 54; *A.*, 1926, 1008.

[39] M. E. Weeks, *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 127; *A.*, 1932, 244.

[40] I. M. Kolthoff, *Chem. Weekblad*, 1924, **21**, 2; *A.*, 1924, ii, 121.

[41] F. Sierra and F. Burriel, *Anal. Fis. Quim.*, 1932, **30**, 441; *A.*, 1932, 924.

[42] L. Szebellédy, *loc. cit.*

[43] H. Roth, *Z. angew. Chem.*, 1926, **39**, 1599; *A.*, 1927, 125.

An indicator of a different type is the *o*-phenanthroline ferrous ion $Fe(C_{12}H_8N_2)_3^{\cdot\cdot}$, which, with the corresponding ferric ion, $Fe(C_{12}H_8N_2)_3^{\cdot\cdot\cdot}$, forms a reversible oxidation–reduction system in which the reduced state has a very intense red and the oxidised state a relatively feeble blue colour, so that there is a marked colour change in the vicinity of 1·1 volts from red almost to colourless or *vice versa*, on oxidation or reduction, respectively. The compounds are not susceptible to destruction by further oxidation, and *o*-phenanthroline ferrous sulphate lends itself particularly for use as indicator in titrations of ferrous ions with dichromate and with ceric sulphate.[48] Since the colour change occurs at a potential more positive than that of the ferrous–ferric system, the addition of complex-forming ions (phosphate or fluoride) is unnecessary.[49] The indicator has also been employed in the titration of ferrocyanide, thallous, arsenious, quadrivalent uranium, oxalate, vanadate, and nitrite ions and hydrogen peroxide by means of ceric sulphate;[50] of vanadate ions alone or in the presence of ferric, chromium, or molybdenum compounds by ferrous sulphate;[51] and of ferrous ions alone or in the presence of vanadium, titanium, chromium, or manganese with ceric sulphate.[52] The use of the nitrophenanthroline ferrous ion as an oxidation–reduction indicator has also been proposed;[53] its oxidation potential is about 0·1 volt more positive than that of the *o*-phenanthroline ferrous ion and so it is doubtful if it can be applied to dichromate titrations.

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[44] J. Knop, *Z. anal. Chem.*, 1929, **77**, 111; 1931, **85**, 253; *A.*, 1929, 670; 1931, 1256; J. Knop and O. Kubelková, *ibid.*, 1929, **77**, 125; *A.*, 1929, 670.

[45] *Idem*, *ibid.*, 1931, **85**, 401; *A.*, 1931, 1261.

[46] *Idem*, *ibid.*, 1929, **77**. 125; *A.*, 1929, 670.

[47] N. H. Furman and J. H. Wallace, *J. Amer. Chem. Soc.*, 1930, **52**, 2347; *A.*, 1930, 1012; A. D. Mitchell and A. M. Ward, "Modern Methods in Quantitative Chemical Analysis," 1932.

[48] G. H. Walden, L. P. Hammett, and R. P. Chapman, *J. Amer. Chem. Soc.*, 1931, **53**, 3908; *A.*, 1931, 1385.

[49] *Idem*, *ibid*, 1933, **55**, 2649; *A.*, 1933, 924.

[50] H. H. Willard and P. Young, *ibid.*, p. 3260; *A.*, 1933, 1025.

In addition to the use in volumetric work of the reversible indicators already described, a number of dyes which undergo *irreversible* oxidation at high positive potentials have also been employed. The application of methyl-orange and methyl-red in bromate titrations is well known,[54] and it has been found that these substances, in addition to methylene-blue, Congo-red,[55] malachite-green and methyl-violet,[56] can be used as internal indicator for the estimation of ferrous and antimonious compounds, oxalates, and quinol by ceric sulphate.

S. G.

4. Microanalysis.

As micro-methods now cover the whole range of analytical chemistry, the advances in only a few selected branches of the subject will be described.

"*Spot*" *Tests.*—The growth and application of spot tests is one of the most important of the recent developments in microchemistry. Originally these were colour tests for various inorganic ions, but many have now been found to be suitable for quantitative work, and they have also been extended to organic chemistry. The tests are generally carried out on a white tile or spot plate, in test-tubes of various sizes, or, in the majority of cases, on thick, close-grained, filter paper. The use of filter paper renders possible the separation of elements by filtration through the pores of the paper, and, in some cases, the simultaneous identification of elements in different zones of the paper owing to variations in diffusion rates or solubility. When the filter paper is impregnated with a solution of the reagent in a volatile solvent, it may often be dried and kept indefinitely, and is obviously especially useful in field work and all tests away from a laboratory. Usually the test is carried out on a single drop of solution, the concentration varying according to the sensitivity of the test from about 1 : 1000 to 1 : 2,000,000; when working in test-tubes, however, as much as 1 ml. of the test solution may sometimes be taken. The limit of identification in spot tests ranges from a few gamma (γ) to a few thousandths γ. Many spot tests are specific when carried out in suitable conditions, and this number is rapidly increasing.

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[51] G. H. Walden, L. P. Hammett, and S. M. Edmonds, *J. Amer. Chem. Soc.*, 1934, **56**, 57; *A.*, 257.

[52] *Idem, ibid.*, p. 350; *A.*, 382.

[53] L. P. Hammett, G. H. Walden, and S. M. Edmonds, *ibid.*, p. 1092; *A.*, 744.

[54] For other suitable indicators, see G. F. Smith and H. H. Bliss, *ibid.*, 1931, **53**, 2091, 4291; *A.*, 1931, 925; 1932, 137.

[55] H. Rathsburg, *Ber.*, 1928, **65**, [*B*], 1663; *A.*, 1928, 1207; H. H. Willard and P. Young, *J. Amer. Chem. Soc.*, 1928, **50**, 1322; *A.*, 1928, 725; N. H. Furman and J. H. Wallace, *ibid.*, 1930, **52**, 1443, 2347; *A.*, 1930, 727, 1012; N. H. Furman, *ibid.*, 1932, **54**, 4235; *A.*, 1933, 43; see also K. Someya, *Z. anorg. Chem.*, 1928, **169**, 293; *A.*, 1928, 387.

[56] R. Vanossi and R. Ferramola, *Anal. Asoc. Quím. Argentina*, 1932, **20**, 96; *A.*, 1933, 138.

Spot tests for organic compounds. A large proportion of spot tests involves the use of organic reagents, and in the investigation of these, certain organic groupings are found to react with certain inorganic ions, and this has led to the development of spot tests for organic radicals by utilising the tests in the reverse manner with the inorganic ion as the reagent. Only a limited number of these tests are suitable, and in general, they are considerably less sensitive than the tests for the inorganic ions. At the same time, however, a number of macro-tests are being applied on the micro-scale with great saving in time and trouble. This spread of spot tests to the whole field of organic qualitative analysis is a most important recent development.

Tests at present available [1] include those for elements present in organic compounds, and also for the following radicals and compounds: NO and NO_2, CO, CHO, $CH_3{\cdot}CO$, $C{:}C{\cdot}CHO$, $C{:}S$ and $C{\cdot}SH$, $CO_2H{\cdot}C{\cdot}C{\cdot}CO_2H$, SO_3H, NH_2, NH, NMe, $ArNH_2$, $N{\cdot}NH_2$, CH_2, NH_2, alcohols, phenols, enols, carbonic acids and their derivatives, and tertiary ring bases. There are also spot tests for a number of individual organic compounds, among which are lactic, oxalic, malic, tartaric, and citric acids, glycerol, tyrosine, pyridine, and others. The sensitivity of these tests ranges downwards from about 100 γ to a few hundredths γ.

It is to be realised that, apart from the organic spot tests mentioned here, there has been a great deal of other work carried out in organic qualitative analysis, notably in the detection of the alkaloids and many pharmaceutical products, mainly using tests involving crystal formation and investigation under the microscope, melting-point determinations under the microscope, sublimation, and other methods of preparative microchemistry.

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[1] (i) F. Feigl; (ii) F. Feigl, V. Anger, and O. Frehden; (iii) F. Feigl and V. Anger, *Mikrochem.*, 1934, **15**, (i) 1, (ii) 15, (iii) 23; *A.*, 790. (iv) F. Feigl, V. Anger, and O. Frehden; (v) F. Feigl, V. Anger, and R. Zappert, *ibid.*, pp. 181, 190; *A.*, 1239; (vi) F. Feigl, V. Anger, and R. Zappert; (vii) F. Feigl and O. Frehden, *ibid.*, **16**, 67, 79; *A.*, 1240; I. M. Korenman, *J. Soc. Chem. Ind.*, 1931, **8**, 508; F. Feigl, "Qualitative Analyse mit Hilfe von Tüpfel reaktionen," 2nd Edn., 1935, 354.

Applications to quantitative analysis. Spot tests have been used for approximate quantitative work by matching colours of spots on paper or a white tile with those from standard solutions, and are useful in some routine investigations and especially in plant and soil work. The accuracy has been investigated for the estimation of copper, silver, lead, manganese, tin, zinc, and magnesium.[2] The following are some of the reagents first used for spot tests which have been successfully applied to accurate colorimetric work:[3] *p*-dimethylaminobenzalrhodanine (Ag), diphenylcarbazone (Hg), sodium diethyldithiocarbamate (Cu), salicylaldoxime (Cu), thioglycollic acid (Fe), αα′-dipyridyl (Fe), diphenylcarbazide (Cr), aurinetricarboxylic acid (Al), dithizone (Pb, etc.), *p*-nitrobenzeneazoresorcinol (Mg).

Occasionally, the precipitations in spot tests are sufficiently complete for use in micro-gravimetric analysis, with low-temperature drying of the product. An example of this is given in the use of rubianic acid as a reagent for the determination of palladium and other metals of the platinum group.[4]

Spot tests for inorganic ions. The number of spot tests of the type first to be developed, those for inorganic ions, is rapidly increasing. Recent work includes the tests mentioned below: A new test for *beryllium*, using *p*-nitrobenzeneazo-orcinol, is sensitive to 0·2γBe in 1 : 200,000 dilution.[5] A sensitive reagent for *boric acid* is *p*-nitrobenzeneazochromotropic acid (Chromotrope 2B),[6] by means of which 0·08γB in 1 : 500,000 dilution can be detected; special precautions are taken in the presence of oxidising anions and of fluorides. A variation in the curcumarin test for *boron* is also described.[7] A test for copper depends on the identification with 8-hydroxyquinoline of the cyanogen liberated by copper salts and potassium cyanide, and is sensitive to 0·4γ.[8] A similar, but somewhat more sensitive, test for *fluorine* than the zirconium–alizarin test is that with zirconium *p*-dimethylaminoazophenylarsonate,[9] whereby the interference of fluorine ions in the test, when used for the identification of zirconium, is utilised, and 0·25γF in 1 : 200,000 dilution may be identified. A simple test for *fluorine* by the etching of glass has also been used as a spot test; 0·5γF in 1 : 100,000 dilution can be identified.[10] When *manganous* salts (in the absence of chromates) are oxidised to permanganate with alkali periodates, invisible amounts of permanganate, down to 0·001γMn in 1 part in 50 million dilution, can be detected by the blue colour on addition of a solution of Arnold's base (tetramethyldiaminodiphenylamine) in chloroform.[11] *Nitrous acid* in the presence of nitrates can be detected down to 0·25γ by means of chrysean (2-aminothiazole-4-thioamide).[12] Useful tests for *selenium* and *tellurium* in the presence of each other are described,[13] whereby 1 part of selenium in the presence of 615 parts of tellurium, or 1 part of tellurium in 100 parts of selenium, can be identified. A specific test for *potassium* among the elements of the fourth and fifth groups of analytical separations, except rubidium and cæsium, uses *p*-dipicrylamine [14] (hexanitrodiphenylamine) as a reagent, and detects 3γK in 1 : 10,000 dilution.

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[2] J. Kisser and K. Lettmayr, *Mikrochem.*, 1932—33, **12**, 235; *A.*, 1933, 137.

[3] H. Fischer, *Angew. Chem.*, 1934, **47**, 685; *A.*, 1191; H. Müller, *Mikrochem.*, 1932—33, **12**, 307; *B.*, 1933, 366; N. Strafford, Institute of Chemistry Publication, 1933 (summary and collected references); L. H. Cooper, *Chem. and Ind.*, 1934, **53**, 830.

[4] H. Wölbling and B. Steiger, *Mikrochem.*, 1934, **15**, 295; *A.*, 1193.

[5] A. S. Komarovsky and N. S. Poluektov, *ibid.*, **14**, 315; *A.*, 746.

[6] *Idem*, *ibid.*, p. 317; *A.*, 745.

[7] N. A. Tananaev and O. A. Kulska, *Ukrain. Chem. J.*, 1934, **9**, 1.

[8] A. S. Komarovsky and N. S. Poluektov, *Z. anal. Chem.*, 1934, **96**, 23; *A.*, 270.

Quantitative Analysis on the "Gamma" Scale.—A considerable amount of accurate work has recently been carried out, mainly applied to biology—in the study of enzymes, in the examination of small plants and animals, and in medical research. Much of this work is volumetric (apart from purely physical methods such as spectrometric and polarographic methods, and others, not dealt with here) and the accuracy is largely obtained by the use of suitable micro-burettes and -pipettes. Linderström-Lang [15] uses home-made capillary *pipettes* of two types, the one to deliver amounts of the order of 0·007 ml., with an error of less than 0·3%, and the other type for larger volumes of the order of 0·03 ml., with an error of less than 0·1%. Both are constructed to deliver the liquid under a pressure of water (20 cm. of water in 7 seconds, and 50 cm. of water in 22 seconds, respectively). Kirk [16] also uses capillary pipettes of capacities ranging from 0·01 to 0·2 ml., and controls the delivery by means of the pressure from a hypodermic syringe.

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[9] F. Feigl and E. Rajmann, *Mikrochem.*, 1932, **12**, 133; *A.*, 1933, 135.

[10] S. K. Hagen, *ibid.*, 1934, **15**, 313.

[11] F. Feigl and L. Weidenfeld; see F. Feigl, *op. cit.*, p. 228.

[12] J. V. Dubský, J. Trtílek, and A. Okáč, *Mikrochem.*, 1934, **15**, 99.

[13] N. S. Poluektov, *ibid.*, p. 32.

[14] *Idem*, *ibid.*, 1933—34, **14**, 265.

[15] K. Linderström-Lang and H. Holter, *Compt. rend. Trav. Lab. Carlsberg*, 1931, **19**, (4), 1.

[16] P. L. Kirk, *Mikrochem.*, 1933—34, **14**, 1; *A.*, 1933, 1262.

The best *micro-burettes* are usually of the Brandt-Rehberg type,[17] *viz.*, a capillary burette, the titrating liquid being above a thread of mercury. The burette is filled or emptied by the operation of a metal screw which raises or lowers the level of the mercury. Linderström-Lang utilises a burette of this type five times as fine as the original, with or without an air gap between the mercury and the titrating liquid according to its stability towards mercury. His burette has a total volume of 0·1 ml. and is graduated in 0·0002 ml.; one-tenth of this can therefore be estimated. Where a micrometer screw is fitted, this is used as a more accurate means of reading the volume than the mercury level. Kirk [16] also uses this type of burette, with capacities of 0·1—0·2 ml., but to simplify matters in the event of breakage, the burette has a detachable tip attached with rubber cement, and fixed outside by means of two brass collars with an open-sided coupling between them to draw the collars together. He also uses a burette of the same type as the syringe pipette, but with a coil spring to prevent back-lash. Schwarz [18] has devised a simpler model of burette without mercury or metal screw (for volumes of the order of 0·2 ml.) with an accuracy of 0·1—0·2%. This is on the wash-bottle principle, and uses suction and blowing for filling and emptying the burette.

On the small scale the *stirring* is usually electrical, one method being to use sealed capillaries, 1—1·5 mm. in length, filled with reduced iron, and to agitate these by means of an electromagnet periodically switched on and off.[15] The stirring may also be carried out by using a very fine-tipped capillary, also agitated electrically by means of an electromagnet through which a 60-cycle A.C. current is passing.[16] In micro-potentiometric work, one of the electrodes may be used as the stirrer, agitated in the same manner.[18]

Some form of adjustable titration table simplifies the use of the above apparatus, which will give very accurate results in the analyses of small amounts of material. The titration is carried out either in micro-beakers consisting of narrow Jena-glass tubes [15] (about 2—2·5 cm. high and 0·4 cm. internal diameter), or in depressions on microscope slides,[16] or, in potentiometric work, in a small drop on a ring made of a metal suitable for the determination.[18] The mean pipetting and titration error as determined by simple titrations is 0·07%,[15] and a little greater in determinations of small cleavages caused by enzymes. Calcium has been determined on amounts of the order of 5γ with errors of less than 1% (a precipitation and filtration also being involved), and the determination applied to the calcium in blood serum or plasma using only about 0·02 ml. of sample.[19] Potentiometric titrations, using a silver electrode for the determination of 1—2γCl, 0·04—0·4γBr, or 4—5γAg, have been carried out with similar errors of less than 1%.[18] Potentiometric determinations of a few γ of iron, lead, and arsenious acid have also been carried out with the same accuracy,[18] and by special refinements of technique the determination of chlorides has been carried to even lower limits of 0·005γ with errors of less than 5%,[20] and of 1—100γ of mercury with errors of the order of 1%.[21]

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[17] P. Brandt-Rehberg, *Biochem. J.*, 1925, **19**, 270.

[18] K. Schwarz, *Mikrochem.*, 1933, **13**, 1; *A.*, 1933, 586.

In the determination of very small amounts of sugars[22] and of ammonia,[23] the micro-beakers are thinly coated with paraffin, so that drops of liquid placed one above the other do not mix until stirred. In the sugar determination, the buffer solution, sugar solution, and iodine are mixed at the bottom of the vessel, and evaporation of iodine is prevented by two films above the surface of the liquid, one of 0·05 ml. of 1·2*N*-sulphuric acid, and one of starch solution in *N*/100-sulphuric acid. The reaction tube can safely be left until the reaction is at an end, then the mixture is centrifuged, and the liquid titrated against *N*/20-thiosulphate, the accuracy being about $2{\cdot}5 \times 10^{-4}$ mg. of glucose.

Ammonia is determined by the film method by mixing the test solution with a drop of 2*N*-caustic soda, and a film of the absorbing acid is placed above. On being left for sufficient time in an incubator at 40°, the ammonia distils into the acid, and the excess acid is titrated with borate (for quantities less than $0{\cdot}2 \times 10^{-6}$ mol.) or alkali (for larger quantities) without causing the drops to mix with the alkali underneath. On amounts of 0·5—2γN, errors of less than 1% were obtained.

Complete micro-Kjeldahl determinations (*i.e.*, digestion included) on organic material containing 4—15γN with a mean error of 1% have been carried out by modifying the usual micro-Kjeldahl procedure.[24]

Gravimetric determinations on this small scale can only be undertaken with a balance of greater sensitivity than the usual Kuhlmann micro-balance. This has been done for simple residue determinations on initial weights of substance varying from 2 to 10γ, with errors of about 0·2%, using Emich's electro-magnetic micro-balance, and also electrical determinations of copper on similar small weights were made with the same accuracy.[25]

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[19] P. L. Kirk, *Mikrochem.*, 1933—34, **14**, 15; *A.*, 1933, 1262.

[20] K. Schwarz and (the late) C. Schlösser, *ibid.*, 1933, **13**, 18; *A.*, 1933, 582.

[21] K. Schwarz and T. Kantor, *ibid.*, p. 225; *A.*, 1933, 799.

[22] K. Linderström-Lang and H. Holter, *Compt. rend. Trav. Lab. Carlsberg*, 1933, **19**, (14), 1.

[23] *Idem, ibid.*, **19**, (20), 1.

[24] P. L. Kirk, *Mikrochem.*, 1934, **16**, 13, 25.

Apparatus.—Advance in micro-methods depends largely on new devices and adaptations for small-scale apparatus. The number of these is so great that only a few can be mentioned. A variety of apparatus for micro-qualitative work using a microscope is described, including an apparatus for qualitative electrolysis under the microscope whereby $0{\cdot}05\gamma$ of lead and copper can be separated and detected.[26] For quantitative electrolysis, a method using a platinum crucible as the electrode to be weighed is useful.[27] Stirring with minute bubbles of gas in electrolysis is also described.[28] A glass instead of a metal cymene heating-bath for use in the Pregl carbon–hydrogen determination is claimed to cause less tarring and clogging of the cymene or decalin.[29] A micro-vacuum desiccator adapted from a large-scale type is described.[30] A spot plate that can be heated is a useful adjunct to qualitative apparatus.[31] A micro-Soxhlet extractor is described;[32] another simple continuous micro-extractor utilises a sintered-glass filter in place of the usual filter-paper cup and syphon device.[33] There is a very large number of designs available for micro-heating blocks for melting-point determinations under the microscope; two recent models both use thermometers rather than a thermocouple for temperature measurement, as being simpler, and, if calibrated on the instrument, just as accurate.[34, 35] Sublimation is one of the most useful methods of extraction and purification on the micro-scale; a number of the methods available are discussed and described.[36] In addition to the micro-burettes already mentioned, a tap-less micro-burette for routine determinations is described.[37] A gauge receiver for use in the Vieböck and Brecher methoxyl determination considerably facilitates transference of the liquid to be titrated.[38]

Quantitative Inorganic Analysis.—No survey of this field is here attempted, but there have been many developments during the past year, both in determinations of single elements applied to special work, mainly biological, and in complicated separations, involving, in general, the Emich filter-stick method. These complicated separations are being applied successfully to a difficult field of analytical work, *viz.*, mineral and rock analysis. J. W. M.

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[25] E. Wiesenberger, *Mikrochem.*, 1931—32, **10**, 10.

[26] H. Alber, *ibid.*, 1933—34, **14**, 219.

[27] H. Brantner and F. Hecht, *ibid.*, p. 27; *A.*, 1933, 1265.

[28] A. Okáč, *ibid.*, 1932—33, **12**, 205; *A.*, 1933, 140.

[29] H. Lieb, *ibid.*, 1933—34, **14**, 263; *A.*, 1934, 425.

[30] W. Münster, *ibid.*, p. 23; *A.*, 1933, 1260.

[31] E. Fränkel, *ibid.*, 1933, **13**, 179; *A.*, 1933, 801.

[32] G. Gorbach, *ibid.*, 1932—33, **12**, 161.

[33] A. R. Lowe (Demonstration at Microchemical Club meeting, March 1934).

[34] L. Kofler, *Mikrochem.*, 1934, **15**, 242.

[35] H. V. A. Briscoe and (Mrs.) J. W. Matthews, Institute of Chemistry Publication, 1934, p. 18.

[36] R. Fischer, *Mikrochem.*, 1934, **15**, 247.

[37] R. Links, *ibid.*, p. 87.

[38] L. Kahovec, *ibid.*, 1933—34, **14**, 341; *A.*, 1934, 790.

B. A. Ellis.
J. J. Fox.
S. Glasstone.
J. W. Matthews.

BIOCHEMISTRY.

THE past year has seen notable advances in our knowledge of the chemical constitution of the sex hormones and of vitamin B_2. The more purely chemical aspects of these subjects are dealt with in the Report on organic chemistry. The identity of vitamin C with ascorbic acid has been fully established, and some progress has been made in determining the nature of vitamin B_1. The mode of breakdown of carbohydrate by the enzyme systems of muscle and yeast has been studied further, and evidence has been supplied in general support of the Embden–Meyerhof schemes reported last year, as well as in defining more closely certain of the stages involved. Attempts have also been made to link the formation of lactic acid with other reactions which also take place in muscle. In amino-acid metabolism a number of somewhat isolated observations have been made, and attention is directed in this Report to a renewed interest in the possibility of carbohydrate formation from fatty acids—a problem which still seems to elude a definite solution. Much valuable work has been done on the nature of the proteolytic enzymes and their substrates, but further clarification is necessary before a short review of the situation is possible. During the year, however, the synthesis has been carried out of substituted diketopiperazines which are claimed to undergo hydrolysis by enzymes—an event of sufficient importance to warrant a special note.

Considerable space has been devoted this year to the question of plant growth-regulating substances, investigations of which are distributed over a number of years. The establishment of auxin as a definite chemical entity has focused the attention of chemists on these growth substances, and some account of the more biological aspects of the subject seems called for. Since the matter has not previously been dealt with in this section of the Report, the customary practice of extending the period under review has been adopted. The practical agricultural importance of legume inoculation also demands reference to the organisms concerned. Interest in the varied and complex problems of the mineral nutrition of plants and the related subject of metabolism continues to increase. The current year's work represents a steady general advancement without isolated spectacular achievement.

ANIMAL BIOCHEMISTRY.

The Secondary Sex Hormones.

Interest in the secondary sex hormones continues unabated, and the elucidation of their chemical structure has made further great progress during the year. Improvements in the methods of separating the different hormones, and the artificial preparation of two of them, justify the hope that the advances in the more purely chemical study of these substances will soon result in similar advances in our knowledge of their biological effects. The chemical constitution of the secondary sex hormones is considered in detail elsewhere in this volume,[1] and it will therefore be sufficient here merely to indicate the suggestions as to structure which are accepted at present.

Testicular Hormone (*Androsterone*).—The structure (I) suggested for the hormone isolated from male urine and from testes[2] has been confirmed by its preparation from *epi*dihydrocholesterol.[3] Like œstrone, it is a hydroxy-ketone, but it differs from the ovarian hormone in being saturated, and in retaining the methyl group of the sterols at C_{10}. A noteworthy difference between androsterone and œstrone is the apparent specificity of the former. As is well known,[4] a large number of substances, all containing the phenanthrene ring system but otherwise differing widely from œstrone, possess the power, sometimes in high degree, of inducing œstrus when injected into immature animals. The formula for androsterone allows the theoretical existence of 128 isomerides, of which Ruzicka and his colleagues prepared four. Two of these, derived from dihydrocholesterol and *epi*dihydrocholesterol, differed in the spatial position of the hydroxy-group but agreed in possessing the *trans*-configuration of rings A and B; the other two, from coprosterol and *epi*coprosterol, had *cis*-configurations of rings A and B but differed similarly with respect to the hydroxy-group. The two *cis*-compounds were without noticeable effect on comb growth in the capon even in doses 15 times as great as those of natural androsterone which sufficed to produce a 20% increase in comb area, and only the substance obtained from *epi*dihydrocholesterol had an activity equal to that of the natural hormone. The specificity, however, is not absolute, and K. Tschernig[5] has actually found a threefold increase in activity to accompany reduction of the keto-group to a secondary alcohol. Moreover, a substance exhibiting androsterone activity (1 capon or mouse unit in 25—100 × 10^{-6} g.) is reported as being obtained by hydrogenation of crude or crystalline follicular hormone (œstrone).[6]

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[1] P. 206.

[2] *Ann. Reports*, 1932, **29**, 241.

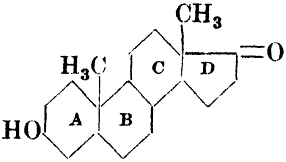
[3] L. Ruzicka, M. W. Goldberg, J. Meyer, H. Brungger, and E. Eichenberger, *Helv. Chim. Acta*, 1934, **17**, 1395; *A.*, 1221.

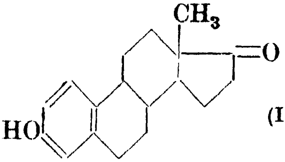
[4] *Ann. Reports*, 1933, **30**, 340.

[5] *Wien. klin. Woch.*, 1934, No. 20.

Two forms of the hormone are suggested by T. F. Gallagher and F. C. Koch,[7] one occurring in the testis itself and the other in urine. They find that the hormone obtained from human male urine is not affected by boiling 3·3% potassium hydroxide solution, whereas hormone prepared from bull testis loses activity in these circumstances, and that the loss is not prevented by urine or hormone prepared from urine. A. A. Adler[8] finds further that in male human urine the hormone is present in an inactive form, extractable by butyl alcohol, and activated by boiling with trichloroacetic acid.

(I.)





(II.)

The Follicular Hormone (*Œstrone*).—The accepted structure of œstrone (II) shows the hormone as differing from androsterone in that ring A is fully aromatic (and has therefore lost the methyl group at C_{10}), the 3-hydroxy-group being therefore phenolic instead of alcoholic.

The excretion of œstrogenic hormone in male urine has been confirmed by B. Zondek,[9] and the isolation and identification of this substance with α-folliculin (œstrone) have been accomplished by E. P. Haussler,[10] and by V. Deulofeu and J. Ferrari.[11] Zondek[9, 12] finds that stallion's urine contains an average of 42,000 mouse units of folliculin per litre, but the non-pregnant mare excretes less than 500 units per litre. Man and other male animals also excrete œstrogenic hormone, though in much smaller amounts—less than 200 units per litre. These findings, in conjunction with the further facts that horse testis yields 54,000 units of follicular hormone per kg., and that implantation of 50 to 100 mg. of testis into spayed mice induces œstrus, are taken to indicate that the testes are concerned in the formation of œstrone by males. Zondek[12] suggests, indeed, that the metabolism of the sex hormones is, in the main, the same for both sexes, and that the male hormone is first produced and then converted into the female hormone.

[6] W. Dirscherl and H. E. Voss, *Naturwiss.*, 1934, **22**, 315; *A.*, 815.

[7] *J. Biol. Chem.*, 1934, **104**, 611; *A.*, 568.

[8] *Nature*, 1934, **133**, 798; *A.*, 815.

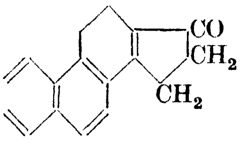
[9] *Ibid.*, p. 209; *A.*, 332.

[10] *Helv. Chim. Acta*, 1934, **17**, 531; *A.*, 702.

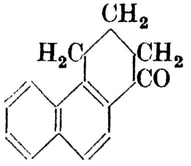
[11] *Z. physiol. Chem.*, 1934, **226**, 192; *A.*, 1269.

[12] *Nature*, 1934, **133**, 494; *A.*, 567.

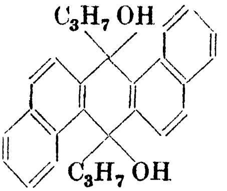
The great range of synthetic œstrogenic substances (all containing the phenanthrene ring system) was discussed last year.[4] The results of Cook and his collaborators have since been published in detail,[13] and another active phenanthrene derivative has been added to the list by J. C. Bardhan,[14] who distilled 2-carboxy-3 : 4-dihydrophenanthrene-1-propionic acid with acetic anhydride and obtained an active substance, $C_{17}H_{14}O$ (probably III or an isomeride).



(III.)



(IV.) 1-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene.



(V.) 9 : 10-Dihydroxy-9 : 10-di-*n*-butyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene.

J. W. Cook, E. C. Dodds, and A. W. Greenwood [15] find that two of their synthetic œstrogenic substances (IV and V) are devoid of androsterone activity, causing no acceleration in comb growth when injected into brown Leghorn capons. They bring about an alteration in the plumage, however, with development of female characteristics.

The increase in the activity of androsterone after reduction of the keto-group is paralleled in the case of œstrone. E. Schwenk and F. Hildebrandt [16] find that reduced œstrone has an activity of 30×10^6 mouse units per g. in the Allen–Doisy test (about three times as great as œstrone), and K. David [17] states that the reduced substance, œstradiol, has about twice the activity of œstrone.

S. L. Cohen and G. F. Marrian [18] report in detail a method for the separation and colorimetric determination of œstrone and œstriol in urine, using a modified Kober reaction [19] (a red colour without green fluorescence on boiling with sulphuric and phenol-sulphonic acids, and dilution with water), with analysis of the colour in a Lovibond tintometer. They state that, although the separation is not strictly quantitative, the method is sufficiently accurate to allow the detection of abnormal amounts of either substance in pregnancy urine.

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[13] J. W. Cook, E. C. Dodds, C. L. Hewett, and W. Lawson, *Proc. Roy. Soc.*, 1934, *B*, **114**, 272; *A.*, 457.

[14] *Nature*, 1934, **134**, 217; *A.*, 1102.

[15] *Proc. Roy. Soc.*, 1934, *B*, **114**, 286; *A.*, 457.

[16] *Naturwiss.*, 1933, **21**, 177; *A.*, 1933, 540.

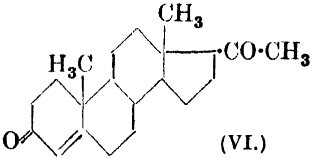
[17] *Acta Brev. Néerl.*, 1933, **3**, 160.

[18] *Biochem. J.*, 1934, **28**, 1603; *A.*, 1269.

[19] *Biochem. Z.*, 1931, **239**, 209.

The International Standard of œstrogenic activity is defined [20] as that contained in 10^{-7} g. of ketohydroxyœstrin (œstrone).

The Corpus Luteum Hormone (*Luteosterone*).—Early in the year under review, the pure corpus luteum hormone was isolated, practically simultaneously, by three groups of workers.[21, 22, 23, 24] There was some difference of opinion at first as to the exact chemical composition of the hormone, and as to its physical properties, but it is now agreed that the main active substance is an unsaturated diketone, $C_{21}H_{30}O_2$, melting at 128°. A second active substance, also an unsaturated diketone, melting at 120° and converted into the first by heat, was considered by Slotta and his collaborators to be a stereoisomeride of the first. Butenandt at first thought it to be $C_{21}H_{32}O_2$, but now [25] considers the two substances to be chemically identical and to differ only in crystalline form and melting point. Luteosterone thus resembles œstrone in existing in polymorphous modifications. The close relationship of the corpus luteum hormone to œstrone, androsterone, and pregnandiol has been shown by A. Butenandt, U. Westphal, and H. Cobler,[26] who succeeded in degrading stigmasterol to a substance (probably VI) with physiological activity only slightly inferior to that of the natural hormone. The substance originally obtained melted at 129—135°, but later work [27] gave a pure diketone of melting point 129°, identical in physical and chemical properties with the natural hormone, and with the same physiological activity. The pure substance has also been obtained from stigmasterol by E. Fernholz,[28] and from pregnandiol by A. Butenandt and J. Schmidt.[29]



(VI.)

Pure luteosterone has not been known long enough for complete information as to its specificity to be obtained, but already a number of interesting observations have been made, tending to the conclusion that it is at least much more specific than œstrone. A curious fact is that reduction of the keto-group attached to the pentamethylene ring reduces the activity very markedly[30]—an effect the opposite of that found with œstrone and androsterone. Equally, reduction at C_3 to the 3-hydroxy-ketone (actually the substance from which the synthetic hormone is obtained by dehydrogenation) gives an inactive compound,[26, 28] and cholestane,[28] though it resembles luteosterone spectroscopically, is without physiological activity. The dihydroxy-compound corresponding to luteosterone is, of course, pregnandiol, which is physiologically inactive. Luteosterone thus differs markedly from the other known sex hormones in that the keto-groups seem to be essential to its activity.

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[20] C. Lormand, *Bull. Soc. Chim. biol.*, 1933, **15**, 1566; *A.*, 1934, 457.

[21] A. Butenandt and U. Westphal, *Ber.*, 1934, **67**, [*B*], 1440; *A.*, 1039.

[22] A. Butenandt, U. Westphal, and W. Hohlweg, *Z. physiol. Chem.*, 1934, **227**, 84; *A.*, 1268.

[23] K. H. Slotta, H. Ruschig, and E. Fels, *Ber.*, 1934, **67**, [*B*], 1270, 1624; *A.*, 931, 1268.

[24] M. Hartmann and A. Wettstein, *Helv. Chim. Acta*, 1934, **17**, 878, 1365; *A.*, 1039.

[25] *Ber.*, 1934, **67**, [*B*], 2088.

[26] *Ibid.*, p. 1611; *A.*, 1268.

[27] *Ibid.*, pp. 1903, 2085.

[28] *Ibid.*, p. 2027.

[29] *Ibid.*, p. 1901.

Origin of the Sex Hormones.—The fact that in all three hormones, the configuration of rings B, C, and D is that of cholesterol and the bile acids is significant evidence that in the animal body they arise by degradation of cholesterol. The relationship between pregnandiol and luteosterone suggests that the former (which could be derived from cholesterol through lithocholic acid) may be the precursor of the corpus luteum hormone *in vivo.* Pregnandiol cannot, however, be the natural precursor of androsterone, for it is a member of the coprostane series, whereas the testicular hormone is derived from *epi*dihydrocholesterol. Ruzicka[3] has suggested that androsterone arises in nature by a process similar to that by which it is obtained *in vitro*—epimerisation of the hydroxy-group of dihydrocholesterol, followed by oxidation of the side chain. J. W. Cook,[31] however, points out that an unsaturated hydroxyketone recently isolated from urine by A. Butenandt[32] may, if the suggested position of the double bond is correct, be the true precursor. The substance can, *in vitro*, be hydrogenated to androsterone.

Little can yet be said of the origin of œstrone, since the stereochemical relations of its ring system are not known, but reference has already been made to Zondek's suggestion that it is derived from androsterone by a process of dehydrogenation and demethylation.

Vitamin B_1.

Although there is not yet absolute agreement as to the identity of the various crystalline vitamin B_1 preparations obtained by different workers, it seems probable that they all contain the same substance but differ in purity. A. G. Van Veen[33] reports a crystalline preparation of oryzanin (from rice polishings) which has a curvative action on polyneuritic rice-birds corresponding to 500 international standard units per mg., an activity which he claims to be greater than that of torulin from bakers' yeast. He describes the substance as containing sulphur, with C 40·7% and H 5·5%. On the other hand, H. W. Kinnersley, J. R. O'Brien, and R. A. Peters [34] point out that an equal activity has been attained in some of their preparations, but that torulin crystals contain 42·2% C, a difference which they regard as significant. As they state that most vitamin B_1 crystals contain inactive material, it follows that small differences in activity by no means necessarily point to complete non-identity of different preparations. Indeed, crystallographic measurements by J. D. Bernal and (Miss) D. Crowfoot [35] suggest that the different groups of workers are actually dealing with the same substance, for they find that crystals from several different sources are substantially identical in form and *X*-ray pattern. They consider that their measurements suggest a conjugated ring structure, with the heavy atoms, sulphur and chlorine, not both at the ends of the molecule.

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[30] A. Butenandt and J. Schmidt, *Ber.*, 1934, **67**, [*B*], 2092.

[31] *Nature*, 1934, **134**, 758.

[32] *Wien. klin. Woch.*, 1934, **47**, 936.

[33] *Nature*, 1934, **133**, 137; *A.*, 333.

A similar identity of the various crystalline preparations of vitamin B_1 is suggested by the most recent work of F. F. Heyroth and J. R. Loofbourow,[36] who find very similar absorption spectra with a number of samples obtained from different laboratories. They state that there is marked correlation between vitamin activity and absorption at or near 2600 Å. The absorption curves, with maxima at 2650 and 2350 Å., resemble those of cytosine, and it is therefore suggested that the vitamin molecule contains a pyrimidine of the cytosine type. The discrepancy between these results and the earlier ones of R. A. Peters and J. St. L. Philpot,[37] which gave the characteristic absorption maximum at 2450 Å., is explained as probably due to the different solvents used.

A. Windaus, T. Tschesche, and R. Grieve,[38] by oxidising vitamin B_1 with nitric acid, have obtained two substances, each containing five carbon atoms. The first of these was isolated as an ethyl ester nitrate, $C_7H_{11}O_5N_3$, the free acid being, therefore, $C_5H_6O_2N_2$. It was not identical with any of the four possible glyoxaline acids of this formula, and it was suggested that it might be a dioxymethylpyrimidine. The second substance, $C_5H_5O_2NS$, gives a methyl ester, loses ammonia and hydrogen sulphide when warmed with alkali, and gives the zinc dust–pine splinter reaction which is held to indicate the presence of a pyrrole ring. The formula (VII) was tentatively suggested for this substance, but the suggestion has since been disproved by K. Niesser,[39] who synthesised a substance of formula (VII). He suggests that the compound isolated by Windaus may be represented by one or other of the formulæ (VIII) and (IX), of which the latter is the more probable. The complete identification of these two substances, which account for ten of the twelve carbon atoms of vitamin B_1, will form an important step in determining the constitution of the vitamin.

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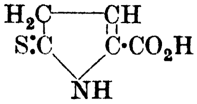
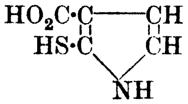
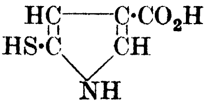
[34] *Nature*, 1934, **133**, 177; *A.*, 333.
[35] *Ibid.*, 1933, **131**, 911; *A.*, 1933, 768.
[36] *Ibid.*, 1934, **134**, 461; *A.*, 1270.
[37] *Proc. Roy. Soc.*, 1933, *B*, **113**, 48; *A.*, 1933, 645.
[38] *Z. physiol. Chem.*, 1934, **228**, 27.

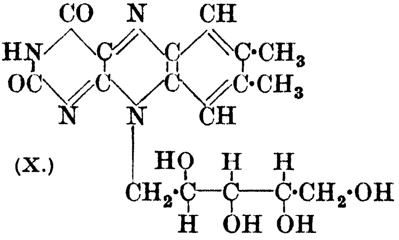

(VII.)


(VIII.)


(IX.)

Vitamin B_2.

Last year it was reported that the flavins, yellow water-soluble dyes extracted from both animal and vegetable sources, possessed intense vitamin B_2 activity, and that lactoflavin from whey was claimed by Kuhn *et al.*[40] to be probably identical with the vitamin. The elucidation of the constitution of the flavins has proceeded so rapidly that, as is described in more detail elsewhere,[41] they are now known to be derivatives of alloxazine, and a substance of constitution represented by formula (X) has been synthesised and stated to be identical with lactoflavin.[42]


(X.)

Flavins have been obtained, though not always in pure crystalline form, from a number of new sources. K. G. Stern[43] has described the isolation of hepatoflavin from horse liver, and has shown that on irradiation it gives products identical in absorption spectra with those from other flavins, and P. Karrer *et al.*[44] give a detailed account of their preparation of hepaflavin, which is identical with lactoflavin in elementary composition, melting point, crystalline form, and absorption spectra. W. Koschara[45] has described uroflavin, from urine, as differing from lactoflavin in elementary composition, containing CH_2O extra, and in melting point (though it does not depress the melting point of lactoflavin), but indistinguishable from it by chromatographic examination. B. C. Guha and H. G. Biswas [46] have obtained renoflavin from ox kidney. F. Plant and K. Bossert [47] have found a chloroform-soluble pigment resembling lumiflavin in the serum and cerebro-spinal fluid of man and rabbit.

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[39] *Ber.*, 1934, **67**, [*B*], 2080.

[40] R. Kuhn, H. Rudy, and T. Wagner-Jauregg, *Ber.*, 1933, **66**, [*B*], 1950; *A.*, 1934, 227.

[41] P. 263.

[42] R. Kuhn and F. Weygand, *Ber.*, 1934, **67**, [*B*], 2084.

[43] *Nature*, 1933, **132**, 784; *A.*, 1934, 97.

[44] *Helv. Chim. Acta*, 1934, **17**, 419; *A.*, 538.

[45] *Ber.*, 1934, **67**, [*B*], 761.

The identity or, alternatively, the exact differences, of these various flavins are still undecided. P. Karrer and K. Schöpp [48] find the flavins of malt, milk, egg, liver, and dandelion to be identical in crystalline form and melting point, whereas Koschara has described uroflavin as non-identical with lactoflavin. It has been suggested [49] that the results of elementary analysis at present indicate non-identity, but the existence of a group of closely related substances, alloxazines substituted in the 9-position. This question of the identity of the flavins bears importantly upon the further question of the nature of vitamin B_2—whether the vitamin is a single naturally occurring flavin, whether, as in the œstrogenic hormone, the activity associated with the vitamin is a property of many substances possessing a common grouping, or whether, as in the case of carotene, the substances isolated are vitamin precursors. This problem cannot yet be regarded as definitely solved, though there is no doubt as to the relationship of the pigments to vitamin B_2 activity. The flavin content of various tissues parallels the vitamin B_2 activity; [50] lactoflavin retains its activity after repeated and varied purifications; [51(a)] and tetra-acetyl lactoflavin also shows activity [52] and retains this activity on regeneration of the original flavin by hydrolysis.[51(b)] But even more impressive is the fact that the synthetic lactoflavin, in doses of 15 mg. per day, produces a growth of 9—10 grams per week in 40-gram rats fed on a diet deficient in vitamin B_2.[53] One may reasonably incline to the view that lactoflavin (or a lactoflavin-protein compound) is itself vitamin B_2 on account of the specificity shown. Both the aromatic methyl groups and the side chain attached to the 9-position of the alloxazine ring are necessary for activity, but as yet complete information as to the degree of specificity in the side chain is lacking. A compound with *n*-amyl in place of the *l*-arabinose of lactoflavin has been synthesised, but no report of its biological activity has yet come to the Reporter's notice.[54] Lactoflavin combines with protein, and according to P. György, R. Kuhn, and T. Wagner-Jauregg,[55] it exists largely in that form in liver and yeast. The protein compound retains vitamin B_2 activity.[56]

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[46] *Current Sci.*, 1934, **2**, 474; *A.*, 1041.

[47] *Klin. Woch.*, 1934, **13**, 450; *A.*, 1022.

[48] *Helv. Chim. Acta*, 1934, **17**, 1013; *A.*, 1233.

[49] K. G. Stern and E. R. Holiday, *Ber.*, 1934, **67**, [*B*], 1442; *A.*, 1041.

[50] E. Adler and H. von Euler, *Svensk Kem. Tidskr.*, 1933, **45**, 276; *A.*, 1934, 226; H. von Euler and E. Adler, *Z. physiol. Chem.*, 1933, **223**, 105; *A.*, 1934, 544.

[51] (*a*) R. Kuhn, H. Rudy, and T. Wagner-Jauregg, *loc. cit.*

(*b*) R. Kuhn and T. Wagner-Jauregg, *Ber.*, 1933, **66**, [*B*], 1577; *A.*, 1933, 1320.

[52] P. György, R. Kuhn, and T. Wagner-Jauregg, *Z. physiol. Chem.*, 1934, **223**, 241; *A.*, 706.

[53] R. Kuhn and F. Weygand, *loc. cit.*

The yellow oxidation enzyme of O. Warburg and W. Christian [57] consists of flavin combined with protein. The reduced leuco-form of the enzyme gives the coloured form and hydrogen peroxide when shaken with atmospheric oxygen; anaërobically it reduces methylene-blue and re-forms the yellow enzyme.[58] H. Theorell [59] finds that the crystalline enzyme, dialysed against dilute hydrochloric acid, is split into two inactive components, pigment and protein. By mixing electrolyte-free solutions of these components, he obtains restoration of enzyme activity. Kuhn,[53] indeed, believes that the biological activity of lactoflavin consists in its assumption of enzymic properties by combination with protein.

One of the biological tests for vitamin B_2 depends on its power of preventing pellagra or pellagra-like dermatitis, and this power is not possessed by flavins. This naturally raises the question of the identity of vitamin B_2 in spite of the close correspondence between the vitamin and flavin by the growth test. C. A. Elvehjem and C. J. Koehn [60] simply deny the identity of the flavins with vitamin B_2, on the ground that colourless liver preparations, after removal of flavins, were highly active in preventing pellagra. They wish, in fact, to retain the name B_2 for the still unknown anti-pellagra factor and to find another term for the activity shown by the flavins. P. György,[61] on the other hand, considers that the old vitamin B_2, the anti-dermatitis factor, consists of the real B_2 (flavin), and a factor, B_6, responsible for the prevention of the pellagra-like dermatitis of rats. He finds that B_6 is not identical with any of the water-soluble vitamins hitherto described. The difference

[54] R. Kuhn and F. Weygand, *Ber.*, 1934, **67**, [*B*], 1939.

[55] *Z. physiol. Chem.*, 1933, **223**, 241; *A.*, 1934, 706.

[56] R. Kuhn and G. Moruzzi, *Ber.*, 1934, **67**, [*B*], 1220; *A.*, 932.

[57] *Ann. Reports*, 1933, **30**, 159.

[58] O. Warburg and W. Christian, *Biochem. Z.*, 1933, **266**, 377; *A.*, 1933, 979.

[59] *Ibid.*, 1934, **272**, 155; *A.*, 1136.

[60] *Nature*, 1934, **134**, 1007.

[61] *Ibid.*, 1934, **133**, 498; *A.*, 569.

between the two workers is obviously one of nomenclature alone, but, the existence of a separate factor having been independently observed, only confusion can result from the multiplication of names. It seems reasonable, in view of the general acceptance accorded to the identification of lactoflavin with vitamin B_2, to adopt the suggestion of György, and to apply the term B_6 to the associated anti-pellagric substance until it, in its turn, has been identified chemically.

It has been suggested on several occasions that vitamin B_2 is an active factor in the liver preparations used for the treatment of pernicious anaemia, and there is no doubt that such preparations are rich in vitamin B_2 or that, conversely, vitamin B concentrates may possess definite curative value in pernicious anaemia. It is worth recording, therefore, that yeast extracts have recently been prepared which possess high curative value but little or no vitamin B_2.[61a]

Vitamin C.

The year 1933 produced very strong evidence that vitamin C is identical with ascorbic acid, but complete acceptance had to await the biological investigation of the synthetic material which had just been obtained by Haworth and his collaborators.[62] Comparative tests on guinea pigs of synthetic *l*-ascorbic acid and highly purified natural material have now demonstrated the complete identity of the substances in physiological as well as in physical and chemical properties.[63] Further accounts of the synthesis of ascorbic acid have been published by the Birmingham workers,[64] and other syntheses by T. Reichstein and A. Grüssner [65] and by F. Micheel, K. Kraft, and W. Lohmann [66] confirm the claim that the synthetic substance is physiologically identical with the natural vitamin C.

It thus appears that *l*-ascorbic acid is, without doubt, vitamin C; but other closely related compounds, which, however, have not yet been found to occur in nature, seem to possess some antiscorbutic activity along with a resemblance to ascorbic acid in readily undergoing reversible oxidation. For instance, K. Maurer and B. Schiedt [67] obtained a substance which they later[68] identified as *d*-arabo-ascorbic acid and showed to have about $\frac{1}{20}$th of the antiscorbutic activity of the vitamin itself.

[61a] C. C. Ungley and G. V. James, *Quart. J. Med.*, 1934, **3** (new series), 523.

[62] *Ann. Reports*, 1933, **30**, 336.

[63] W. N. Haworth, E. L. Hirst, and S. S. Zilva, *J.*, 1934, 1155; *A.*, 1091; V. Demole, *Biochem. J.*, 1934, **28**, 770; *A.*, 934.

[64] *J.*, 1934, 62, 1192; *A.*, 279, 1091.

[65] *Helv. Chim. Acta*, 1934, **17**, 331; *A.*, 510.

[66] *Z. physiol. Chem.*, 1934, **225**, 13; *A.*, 869.

[67] *Ber.*, 1933, **66**, [*B*], 1054; *A.*, 1933, 936.

The occurrence of toxic symptoms following the administration of excessive amounts of vitamin D has naturally directed attention to the possibility of hypervitaminosis in other cases. G. Gothlin[69] finds that at least 1·33 mg. of crystalline ascorbic acid are required daily to protect guinea pigs completely against pre-scorbutic changes in the molar teeth, and calculates the minimum daily dose for adult men of 60 kg. at 19—27 mg. (3·16—4·5 mg. per kg.). These figures are rather higher than those previously reported for the protection of guinea pigs[70] (0·5—1·0 mg. per day), but the test used is more rigorous. On this basis the doses which E. Kramár[71] found to be well tolerated by infants (15—50 mg.) cannot be considered excessive, but V. Demole[72] found no ill effects to follow the administration to guinea pigs of amounts up to 2·5 g. per kg. of body weight for six days.

The mode of action of vitamin C is still by no means clear, though the availability of the pure substance will undoubtedly facilitate the attack on this problem. The tendency is naturally to examine ascorbic acid with reference to various enzyme systems and especially oxidising systems in view of the ease with which it undergoes reversible oxidation. J. H. Quastel and A. H. M. Wheatley[73] find that slices of rat liver or of scorbutic guinea pig liver (but not always of normal guinea pig liver), suspended in glycerophosphate–Locke solution containing sodium butyrate or crotonate, give an increased production of acetoacetic acid and an increased oxygen usage when ascorbic acid is added. Further, they find that ascorbic acid prolongs the steady uptake of oxygen by liver slices. The oxidation of fatty acids by liver slices is largely inhibited by iodoacetic acid, and this inhibition is partly neutralised by ascorbic acid, although there is no evidence of a chemical reaction between the vitamin and iodoacetic acid analogous to that between the latter and glutathione. Quastel and Wheatley suggest that ascorbic acid plays some part in maintaining the general respiratory metabolism, on the integrity of which the oxidation of fatty acids (and, presumably, of other substrates) must ultimately depend. Ascorbic acid has also been described as having an activating effect on proteases of the cathepsin type [74] (from which the natural activators had been removed by acetone), increased by $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, and $Ca^{\cdot\cdot}$, as well as on arginase [75] in presence of $Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ (dehydroascorbic acid acts similarly on arginase). On the other hand, wheat amylase and catalase are said to be inhibited by ascorbic acid,[74] as is tyrosinase with respect to tyrosine, 3 : 4-dihydroxyphenylalanine, and *dl*-adrenaline.[76]

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[68] *Ber.*, 1934, **67**, [*B*], 1239; O. Dalmer and T. Moll, *Z. physiol. Chem.*, 1933, **222**, 116; *A.*, 1934, 227.

[69] *Nature*, 1934, **134**, 569; *A.*, 1271.

[70] *Ann. Reports*, 1932, **29**, 253.

[71] *Deut. med. Woch.*, 1933, **59**, 1428; *A.*, 1934, 1271.

[72] *Biochem. J.*, 1934, **28**, 770; *A.*, 934.

[73] *Ibid.*, p. 1014; *A.*, 934; cf. D. C. Harrison, *ibid.*, 1933, **27**, 1501; *A.*, 1933, 1340.

The Breakdown of Carbohydrate to Lactic Acid in Muscle.

The important Embden–Meyerhof theory of the chemical changes involved in the conversion of carbohydrate into lactic acid by muscle or into ethyl alcohol by yeast was reviewed in some detail last year.[77] Since that time, a considerable volume of evidence has appeared in support of the theory, although there are indications that the series of reactions proposed for the formation of lactic acid in muscle may not represent all the changes taking place. The crux of the matter is, of course, the position of methylglyoxal, which Meyerhof ignores as an unimportant by-product (or possibly,[78] when it is isolated, an artefact) from triose-phosphoric acid. This view, however, is difficult to reconcile with a number of experimental observations, and a dual or multiple route has been suggested by several workers.[79, 85]

The isolation of methylglyoxal from muscle pulp has frequently been reported, and, especially when the glyoxalase system has been inhibited (by anti-glyoxalase, or by iodoacetic acid), the amount produced represents a considerable fraction of the added substrate (hexose-diphosphoric acid or glycogen). Claims of this nature have recently been renewed by N. Arayama,[80] who reviews the earlier papers on the subject. Dealing with lactic acid fermentation by yeast, E. Auhagen and T. Auhagen [81] confirm the production of methylglyoxal and state that it is a primary product of the reaction and is not an artefact due to the addition of " fixing " reagent (2 : 4-dinitrophenylhydrazine). Also using yeast, M. Kobel and H. Collatz [82] find that, under conditions shown to be optimal for the production of methylglyoxal from hexose-diphosphoric acid, only lactic acid is formed from added glyceraldehyde-phosphoric acid. They conclude that methylglyoxal is formed from sugars, but not from this particular triose-phosphoric acid—a conclusion definitely suggestive of a dual route.

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[74] H. von Euler, P. Karrer, and F. Zehender, *Helv. Chim. Acta*, 1934, **17**, 157; *A.*, 461 (cf. *A.*, 1933, 873).

[75] P. Karrer and F. Zehender, *ibid.*, p. 737; *A.*, 1034.

[76] E. Abderhalden, *Fermentforsch.*, 1934, **14**, 367; *A.*, 1138.

[77] *Ann. Reports*, 1933, **30**, 327.

[78] *Ann. Inst. Pasteur*, 1934, **53**, 221; *A.*, 1137.

[79] M. Jowett and J. H. Quastel, *Biochem. J.*, 1934, **28**, 162.

[80] *J. Biochem. Japan*, 1934, **20**, 371; see also, E. Aubel and E. Simon, *Compt. rend. Soc. Biol.*, 1933, **114**, 905; *A.*, 1934, 807.

[81] *Biochem. Z.*, 1934, **268**, 247; *A.*, 562.

[82] *Ibid.*, p. 202; *A.*, 449.

One of the strongest arguments in favour of the non-participation of methylglyoxal in lactic acid formation is the finding that dialysed muscle extracts, which contain no glutathione (co-enzyme of glyoxalase), still produce lactic acid on addition of a magnesium salt and adenylic acid pyrophosphate. This argument still holds, at least as showing that methylglyoxal is not an obligate intermediate. The fact that glutathione is destroyed *in vitro* by iodoacetic acid, which also inhibits lactic acid production, meets the claim that iodoacetic acid acts in other ways [83] than by preventing glyoxalase activity. This claim is supported by certain facts to be reported later, and by the observation that glycolysis in shed blood is inhibited by iodoethyl alcohol, which, however, does not form hydriodic acid with glutathione *in vitro*.[84] Nor is it overthrown by the fact that added glutathione can prevent iodoacetate poisoning in the isolated frog's ventricle and can even cause recovery from the poisoning when the ventricle has almost ceased to respond to stimulation.[85]

R. Gaddie and C. P. Stewart [85] have advanced evidence which supports the Embden–Meyerhof scheme of lactic acid production, but which again is suggestive of a dual route. Using the isolated frog's ventricle, exhausted of available carbohydrate in an atmosphere of nitrogen, they found (confirming N. Freund and W. König,[86] and their own earlier work with A. J. Clark [87]) that the power of contracting on stimulation was entirely restored by glucose. Incidentally, it was also restored by mannose, but not by galactose, fructose, or by any pentose or disaccharide. It was a reasonable assumption that intermediates in the conversion of glucose into lactic acid should also restore the power of responding to stimulation, and actually a partial restoration was obtained by addition to the perfusion fluid of sodium pyruvate with sodium glycerophosphate, though neither substance was effective alone. On the other hand, a partial, but rather better restoration was given by methylglyoxal: this at least shows that, however methylglyoxal is formed, the energy of its conversion into lactic acid is utilisable by the contractile processes. In both cases the partial recovery became full recovery on further addition of glucose. While, then, no evidence suggests that the chain of reactions required by the Embden–Meyerhof scheme does not take place, there is definite evidence that other reactions, also leading to lactic acid production, may occur simultaneously—or perhaps under slightly different conditions.

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[83] *Ann. Reports*, 1933, **30**, 330.

[84] D. M. Mowat and C. P. Stewart, *Biochem. J.*, 1934, **28**, 774; *A.*, 912.

[85] R. Gaddie and C. P. Stewart, *J. Physiol.*, 1934, **80**, 457.

[86] *Arch. exp. Path. Pharm.*, 1927, **129**, 193.

[87] *J. Physiol.*, 1932, **75**, 321.

The first stage in the conversion of fructose-diphosphoric acid into lactic acid is the splitting of the six-carbon chain with the production of two molecules of triose-phosphoric acid. It has already been shown [88] that one component of the synthetic (racemic) glyceraldehyde-phosphoric acid is capable of conversion by muscle extracts into phosphoglyceric and glycerophosphoric acids—the second stage in lactic acid formation—or, under different conditions, into pyruvic and glycerophosphoric acids—the third stage. Early this year, O. Meyerhof and K. Lohmann [89] found that hexose-diphosphate, added in low concentration to co-enzyme-free muscle juice or yeast maceration juice, was rapidly converted into a triose-phosphoric acid (in yields up to 60%) which closely resembled, but was not identical with, synthetic glyceraldehyde-phosphoric acid. They suggested that it was slightly impure dihydroxyacetone-phosphoric acid, and later [90] found that it was indeed identical with the synthetic substance, which was prepared by W. Kiessling [91] and found by him to be fermentable. This ester is readily hydrolysed by 0·5N-sodium hydroxide to lactic and phosphoric acids, and by acid to methylglyoxal and phosphoric acid. Meyerhof and Lohmann found that, whether they used hexose-diphosphoric acid or the synthetic dihydroxyacetone-phosphoric acid as substrate, there was, in the presence of enzyme, the same ultimate equilibrium between the two esters, and it was possible to prepare hexose-diphosphoric acid from the triose ester. The effect of temperature on the equilibrium was the same whether the initial substrate was natural or synthetic dihydroxyacetone-phosphoric acid or hexose-phosphoric acid. The equilibrium was disturbed by potassium cyanide and by sodium bisulphite, the presence of the latter allowing the isolation of dihydroxyacetone-phosphoric acid (from hexose-diphosphoric acid) in 90% yield. The enzyme concerned in this reaction (zymohexase) is water-soluble, moderately thermo-stable, and is unaffected by iodoacetate, fluoride, or oxalate.[92] A point of considerable interest is that the conversion of hexose-diphosphoric acid into two molecules of dihydroxyacetone-phosphoric acid is an endothermic reaction, the measured heat of reaction being given as − 33·5 g.-cals. per gram,[93] or − 6000 g.-cals. per gram-molecule,[94] of the hexose-diphosphoric acid.

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[88] *Ann. Reports*, 1933, **30**, 329.

[89] *Naturwiss.*, 1934, **22**, 134; *A.*, 560.

[90] *Ibid.*, p. 220; *A.*, 807.

[91] *Ber.*, 1934, **67**, [*B*], 868; *A.*, 754.

[92] O. Meyerhof and K. Lohmann, *Biochem. Z.*, 1934, **271**, 89; *A.*, 927.

It has thus been shown that both the triose-phosphoric acids to be expected from hexose-diphosphoric acid are capable of yielding lactic acid in the presence of muscle extracts, and of doing so by way of the intermediates suggested by Embden and his colleagues. The work of Meyerhof and Lohmann suggests that dihydroxyacetone-phosphoric acid is the main triose ester to be formed *in vivo*, and in its case its production from and conversion into hexose-diphosphoric acid have also been demonstrated. This does not yet appear to have been done for glyceraldehyde-phosphoric acid, though it has been shown that glyceraldehyde is capable of yielding glycogen in the animal body.[95]

The breakdown of phosphoglyceric acid to pyruvic acid has been further studied. The enzymic breakdown occurs only in the presence of adenylic acid pyrophosphate and a magnesium salt,[96] and in the absence of these a phosphopyruvic acid is obtained which exists in enzymic equilibrium with phosphoglyceric acid, and which is hydrolysed by muscle extract containing co-enzyme to pyruvic and phosphoric acids. The degradation of *l*-phosphoglyceric acid to pyruvic acid by fresh bottom yeast has been confirmed by W. Schuchardt and A. Vercelloni,[97] and C. Neuberg and M. Kobel[98] have observed a similar reaction in the presence of pulped germinated peas and beans. A. E. Braunstein has observed it also in the presence of hæmolysed (but not intact) erythrocytes from rabbits and pigeons. It is evident, therefore, that the responsible enzyme is widely distributed, a fact which lends further support to the supposition that the conversion of phosphoglyceric acid into pyruvic acid is a general step in carbohydrate breakdown.

The simple view that the enzymic hydrolysis of phosphagen to creatine and phosphoric acid provides the energy for muscular contraction, and that the resynthesis of phosphagen is a recovery process at the expense of carbohydrate breakdown, is becoming less satisfactory as a result of recent work. E. Lundsgaard[99] finds that in muscle poisoned by iodoacetic acid the energy utilisation is greater than can be accounted for by the phosphagen breakdown, and a similar conclusion can be reached from figures given for anaërobic cardiac muscle by A. J. Clark, M. G. Eggleton, and P. Eggleton.[1] Lundsgaard considers that the extra energy cannot be accounted for by utilisation of adenylic acid pyrophosphate, since this only becomes perceptible at a late stage after considerable fatigue, and he failed to find anaërobic synthesis of phosphagen or hydrolysis of adenylic acid pyrophosphate. He considers, in fact, that phosphagen breakdown is a recovery process.

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[93] O. Meyerhof and K. Lohmann, *Naturwiss.*, 1934, **22**, 452; *A.*, 1034.

[94] *Idem*, *Biochem. Z.*, 1934, **273**, 73; *A.*, 1261.

[95] R. Stoher, *Z. physiol. Chem.*, 1934, **224**, 229; *A.*, 919.

[96] K. Lohmann and O. Meyerhof, *Biochem. Z.*, 1934, **273**, 60; *A.*, 1261.

[97] *Ibid.*, 1934, **272**, 434; *A.*, 1260.

[98] *Ibid.*, p. 457; *A.*, 1260.

[99] *Ibid.*, 1934, **269**, 308; *A.*, 685.

One may note here that hitherto no chemical reaction has been discovered which can at present be regarded as initiating muscular contraction; first, lactic acid formation was shown to be a recovery process, and now phosphagen hydrolysis is placed in the same category. It seems that more attention might well be given to the views of Ritchie,[2] who suggests that the contractile processes of muscle are physical (he regards the contracted as the true resting state of muscle, and the relaxed as the condition in which tension is being maintained, thus reversing the usual notion), and that all the known chemical reactions are recovery processes.

A similar conception of phosphagen hydrolysis as a secondary reaction is instinct in the suggestion of K. Lohmann,[3] who considers that the production of creatine and phosphoric acid from phosphagen is not due to a specific phosphatase, but is the resultant of two reactions :

Adenylic acid pyrophosphate = adenylic acid + $2H_3PO_4$.

Adenylic acid + 2 phosphagen = adenylic acid pyrophosphate + creatine.

In accordance with this view he finds [4] that, though adenylic acid and phosphagen separately are inactive as co-enzyme of lactic acid formation, a mixture of the two exhibits the activity of adenylic acid pyrophosphate. J. K. Parnas and P. Ostern [5] accept Lohmann's view of the connexion between adenylic acid pyrophosphate and phosphagen breakdown, but go further, considering the breakdown of carbohydrate also to be coupled with these reactions and to bring about the resynthesis of phosphagen :

(1) Adenylic acid pyrophosphate + glycogen + water = adenylic acid + fructose diphosphoric acid.

(2) Adenylic acid + phosphocreatine = adenylic acid pyrophosphate + creatine.

(3) Creatine + fructose diphosphoric acid = phosphocreatine + lactic acid.

Recently, the same authors with T. Mann [6] have adduced evidence that the resynthesis of phosphagen is particularly associated with the conversion of phosphoglyceric acid into pyruvic acid. Phosphoglyceric acid, added to muscle pulp poisoned with iodoacetic acid, prevents ammonia formation which occurs in presence of free adenylic acid but not of the pyrophosphate, and also allows the formation of phosphagen. Resynthesis of phosphagen in these circumstances is not permitted by addition of free phosphate or of any of the other intermediates in the Embden–Meyerhof series. Moreover, addition of pyruvic acid and phosphate together to fluoride-poisoned muscle pulp stops ammonia formation and allows synthesis of adenylic acid pyrophosphate (and therefore, according to Lohmann, of phosphagen). It is suggested, therefore, that the real intermediary phosphate carrier is phosphopyruvic acid, and that the phosphate from this substance is transferred to creatine and thence to adenylic acid. Reaction (3) above thus includes, as one of its stages, the reaction :

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[1] *J. Physiol.*, 1932, **75**, 332.

[2] *Ibid.*, 1933, **78**, 322.

[3] *Biochem. Z.*, 1934, **271**, 264; *A.*, 1034.

[4] *Ibid.*, p. 278; *A.*, 1033.

[5] *Nature*, 1934, **134**, 627.

[6] *Ibid.*, p. 1007.

Phosphoglyceric acid + creatine (= phosphopyruvic acid + creatine + H_2O) = pyruvic acid + phosphocreatine + H_2O.

Parnas and his colleagues point out that their experiments indicate an inhibitory effect of iodoacetic acid on the earlier stages of carbohydrate breakdown, *i.e.*, on some reaction prior to the formation of phosphoglyceric acid. Meyerhof and Lohmann [92] have found that iodoacetic acid does not interfere with the formation of triosephosphoric acid from hexose-diphosphoric acid. It follows that iodoacetic acid inhibits either the formation of hexose-diphosphoric acid or the conversion of dihydroxyacetone-phosphoric acid into glycerophosphoric and phosphoglyceric acids. Since Parnas and Ostern (*loc. cit.*) have found that in the iodoacetic acid poisoned heart adenylic acid accumulates with formation, not of free phosphate, but of carbohydrate phosphoric esters, it seems that iodoacetic acid must act in the latter of these reactions.

There are, of course, difficulties in the complete acceptance of the suggestions of Parnas, though possibly they may be removed when a more detailed exposition appears. In particular it is not easy to reconcile Parnas's series of reactions with the long continuance of muscular contraction after poisoning with iodoacetic acid. Aërobically, cardiac muscle, poisoned with iodoacetate, can continue to contract for some hours without lactic acid formation and with maintenance of the usual phosphagen concentration.[7] It would appear, therefore, that phosphagen can be resynthesised at the expense of other—presumably exothermic—reactions than lactic acid formation, and that, although the phosphate transference postulated by Parnas may occur normally, it is not essential to the process of contraction. This verdict is probably justified in spite of the admitted differences between cardiac and skeletal muscle (though it is doubtful whether any of them are really fundamental).

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[7] A. J. Clark *et al.*, *loc. cit.*

To the number of these differences, one more has recently been added. F. Beattie, T. H. Milroy, and R. W. M. Strain[8] have obtained, from the heart of the rabbit, cat, dog, ox, and horse, a substance which, on the basis of chemical composition and behaviour towards acid, they describe as different from the adenylic acid pyrophoshate of skeletal muscle, and as resembling a dinucleotide composed of one molecule of adenosine-diphosphoric acid and one molecule of adenosine-triphosphoric acid. Only about 60% of its total phosphorus is labile (as compared with 67% in the case of the substance from skeletal muscle), and it is stated to be more powerful than the ordinary adenylic acid pyrophosphate in reactivating inactive extracts of both voluntary and cardiac muscle. The same substance has apparently been obtained from fresh heart by P. Ostern,[9] who described the isolation of a diadenosine-pentaphosphoric acid, but failed to obtain it from pig heart, which yielded adenosine-5-phosphoric acid instead.

The Metabolism of Amino-acids.

Cystine and Methionine.—H. S. Loring, D. Dorfmann, and V. du Vigneaud[10] have confirmed the observation that *d*-cystine does not promote growth, but find that *meso*cystine can be used as the sole source of cystine. They suggest that this is due to reduction with liberation of *l*-cysteine. Corresponding to this difference in growth-promoting power, the cystine isomerides show differences in the ease with which they are oxidised in the animal body.[11] When the lævo-acid is fed to rabbits, about 80% of the extra urinary sulphur is in the form of sulphate, but with the dextro-acid only about 45%. Racemic and *meso*cystine give intermediate results. Similar results have recently been reported by J. A. Stekol,[12] who finds that dogs excrete as sulphate 40% of the sulphur from *dl*-cystine but only 12% of that from *l*-cystine. V. du Vigneaud, H. S. Loring, and H. A. Craft[13] find that homocystine, *dl*-methionine, and *S*-methylcystine are all readily oxidised by rats, the percentage of the extra urinary sulphur appearing as sulphate being practically the same for the first two. *S*-Methylcystine, however, does not stimulate growth.

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[8] *Biochem. J.*, 1934, **28**, 84, 90; *A.*, 431.

[9] *Biochem. Z.*, 1934, **270**, 1; *A.*, 677.

[10] *J. Biol. Chem.*, 1933, **103**, 399; *A.*, 1934, 212.

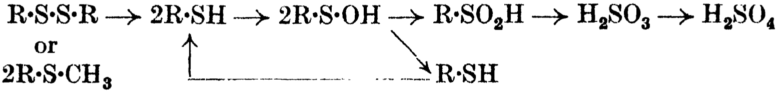
[11] V. du Vigneaud, H. A. Craft, and H. S. Loring, *ibid.*, 1934, **104**, 81; *A.*, 322.

[12] *Ibid.*, 1934, **107**, 225.

[13] *Ibid.*, 1934, **105**, 481; *A.*, 921.

The ready oxidation of *dl*-methionine has been confirmed [14, 15] and the fact that α-benzoylmethionine is not attacked by the animal body is reported by R. W. Virtue and H. B. Lewis,[15] who suggest that methionine is demethylated to homocysteine. These authors also find that the urinary substance (after methionine feeding) giving the cyanide–nitroprusside test [16] does not respond to the Sullivan test for cystine.

N. W. Pirie [17] has begun a study of the intermediate stages in the oxidation of sulphur-containing amino-acids, having succeeded in demonstrating their oxidation to sulphate by slices of rat liver and kidney. He finds that cystine is oxidised only after reduction to cysteine; glutathione only after hydrolysis; methionine is oxidised rather slowly, and during the oxidation the fluid contains a substance which gives the nitroprusside reaction; ethylcysteine is oxidised slowly and, curiously, ergothionine not at all. Pirie suggests, therefore, that in all cases oxidation starts from a sulphydryl compound the formation of which by reduction or dealkylation is the first stage. He suggests, tentatively, the following series of reactions, of which the third has already been shown to proceed spontaneously at body p_H :



$$\begin{array}{l} \mathrm{R{\cdot}S{\cdot}S{\cdot}R} \rightarrow 2\mathrm{R{\cdot}SH} \rightarrow 2\mathrm{R{\cdot}S{\cdot}OH} \rightarrow \mathrm{R{\cdot}SO_2H} \rightarrow \mathrm{H_2SO_3} \rightarrow \mathrm{H_2SO_4} \\ \quad \text{or} \\ 2\mathrm{R{\cdot}S{\cdot}CH_3} \qquad \qquad \mathrm{R{\cdot}SH} \end{array}$$

V. du Vigneaud *et al.*[18] have reported the synthesis of pentocystine, $[HO_2C{\cdot}CH(NH_2){\cdot}(CH_2)_3{\cdot}S{\cdot}]_2$, and homomethionine, $CH_3{\cdot}S{\cdot}(CH_2)_3{\cdot}CH(NH_2){\cdot}CO_2H$, but so far no report of their metabolic effects has appeared.

Tryptophan.—It is interesting in view of the specific growth effect of *l*-cystine, that the stereoisomeric forms of tryptophan are equally effective in promoting the growth of rats.[19] Acetylation, however, introduces specificity, since acetyl-*d*-tryptophan is not utilised as a growth promoter (possibly because it is not easily hydrolysed in the body). Neither *d*-tryptophan nor its acetyl derivative leads to kynurenic acid excretion, and acetylation considerably

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[14] J. A. Stekol and C. L. A. Schmidt, *Univ. California Pub. Physiol.*, 1933, **8**, 31; *A.*, 1934, 440.

[15] *J. Biol. Chem.*, 1934, **104**, 59; *A.*, 322.

[16] *Ann. Reports*, 1933, **30**, 333.

[17] *Biochem. J.*, 1934, **28**, 305; *A.*, 440.

[18] V. du Vigneaud, H. M. Dyer, C. B. Jones, and W. J. Patterson, *J. Biol. Chem.*, 1934, **106**, 401; *A.*, 1094.

[19] C. P. Berg, *ibid.*, 1934, **104**, 373; *A.*, 440.

reduces the amount of kynurenic acid formed from the lævo-isomeride. L. C. Bauguess and C. P. Berg[20] found further that β-3-indolylacrylic acid and α-oximino-β-3-indolylpropionic acid were both without effect on growth and were not converted into kynurenic acid by the rabbit. Racemic β-3-indolyl-lactic acid, however, both supported growth and led to kynurenic acid excretion. Part of the amount fed was recovered from the urine (more of the *l*-compound than of the *d*-, which suggests a greater efficiency of the *d*-acid). β-3-Indolylpyruvic acid was also converted into kynurenic acid, and was not recoverable from the urine. The same authors[21] found that amides of *l*-tryptophan support growth and yield kynurenic acid. These results suggest, of course, that, whatever may be the mechanism of the growth-promoting action of tryptophan, it involves the formation of an optically inactive compound, presumably the corresponding keto-acid.

R. S. Alcock,[22] indeed, points out that kynurenic acid formation is probably a side or "shunt" reaction (possibly a detoxicating mechanism) dealing with excess of tryptophan by way of indole-pyruvic acid; the ease with which various tryptophan derivatives yield kynurenic acid is no more than a measure of the ease with which they are converted into the keto-acid. He finds that rats on a tryptophan-deficient diet do not grow when tryptophan is injected, but do grow when given small daily doses of the anterior pituitary growth hormone (0·1—0·15 ml. of the extract per day, injected). He suggests that the animal can synthesise tissue proteins without receiving tryptophan in the diet, but that it requires tryptophan for the synthesis, in the liver, of some substance essential to life.

Histidine.—S. Edlbacher and M. Neber,[23] in a further study of the breakdown of histidine by histidase, consider that the reaction involves the opening of the glyoxaline ring with addition of $2H_2O$ and formation of ammonia and ω-formylglutamine. The product of enzyme action is hydrolysed by sodium hydroxide to ammonia, formic acid, and glutaminic acid, and on oxidation with hydrogen peroxide it gives succinic acid semialdehyde, as does glutaminic acid.

Amino-acid Anhydrides.—It is perhaps invidious to single out any one item from the mass of interesting work on peptides and their hydrolysis by enzymes, but the subject as a whole seems hardly ready for review. A point of particular interest, however, is the possibility of the occurrence of diketopiperazines in the protein molecule. The great obstacle to the acceptance of this possibility has been the failure of proteolytic enzymes to hydrolyse diketopiperazines. Recently, however, K. Shibata [24] has obtained four substituted diketopiperazines which underwent enzymic hydrolysis, and two of these contained only naturally occurring amino-acids. Glycyldiaminopropionic anhydride, $NH<\substack{CHR{-}CO\\CO\cdot CHR'}>NH$ ($R = H$, $R' = CH_2\cdot NH_2$), and diaminopropionic anhydride ($R = R' = CH_2\cdot NH_2$) were hydrolysed by pepsin; and glycylglutaminic anhydride ($R = H, R' = CH_2\cdot CH_2\cdot CO_2H$) and asparagine anhydride ($R = R' = CH_2\cdot CO_2H$) were hydrolysed by trypsin, cathepsin, and papain.

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[20] *J. Biol. Chem.*, 1934, **104**, 675, 691; *A.*, 554.

[21] *Ibid.*, 1934, **106**, 615; *A.*, 1252.

[22] *Biochem. J.*, 1934, **28**, 1721.

[23] *Z. physiol. Chem.*, 1934, **224**, 261; *A.*, 920.

Indirect Calorimetry.

Last year, E. P. Poulton [25] amplified a previous note [26] on certain errors in the measurement of heat production by calculation from the gaseous exchange using the Zuntz–Schumburg factors. He found that, though the heat produced was proportional to the carbon dioxide, the correlation between heat production and oxygen usage was bad. There is, he says, considerable variation in the oxygen consumption—the heat and the carbon dioxide production remaining constant—but on the whole the amount of oxygen used is unexpectedly small at R.Q. above about 0·8, and unexpectedly high below that level. He suggests that under basal conditions there is actually a constant combustion ratio of carbohydrate to fat, and that the errors in calculating the heat production from the oxygen consumption are to be explained by the use of oxygen for partial oxidations or its liberation in reductions, whereas the carbon dioxide production represents complete oxidations.

One of the most obvious of incomplete oxidations is, of course, the formation of carbohydrate from fat, and the vexed question of whether this does or does not occur in the animal body still receives attention. The great criticism which is directed against all attempts to prove this conversion is that they depend upon measurements of the R.Q., and that even if the accuracy of the measurements be granted, alternative explanations may still be possible. In adipose subjects undergoing dietetic weight reduction, where conditions for sugar formation from fat ought to be ideal, V. Forbech and F. Leegaard [27] found that the carbohydrate metabolised frequently exceeded the intake, and that the low R.Q. supported the idea that fat was converted into carbohydrate. In both man and the pig, following high fat diets, Hawley *et al.*[28] found values of the R.Q. too low to be accounted for by ketosis or by carbohydrate formation from protein or glycerol. (F. H. Lashmet and L. H. Newburgh [29] find that, contrary to the usual view, only 30% or less of glycerol is converted into glucose.) They found considerable individual variation, the occurrence of a low R.Q. depending less on the amount of fat in the diet or the carbohydrate/fatty acid ratio than on the tolerance of the subjects. They point out that other explanations than that of glucose formation from fat are conceivable, and direct attention to the effect of cold in producing a low R.Q. and to the specific dynamic action of butter fat.

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[24] *Acta Phytochim.*, 1934, **8**, 173; *A.*, 1260.

[25] *Proc. Roy. Soc. Med.*, 1933, **26**, 1591.

[26] T. W. Adams and E. P. Poulton, *J. Physiol.*, 1932, **77**, (Proc.) 1.

[27] *Acta Med. Scand.*, 1934, **81**, 351; *A.*, 1025.

J. M. Peterson [30] has compared the R.Q. in decerebrate and in decerebrate eviscerate cats, with corrections for displaced carbon dioxide. He finds that the true oxidative R.Q. in decerebrate eviscerate cats is about 0·825, and calculates the R.Q. of the removed viscera to be 0·69, a value which he considers to be associated with liver gluconeogenesis.

The subject of carbohydrate production from fat has been critically reviewed by H. H. Mitchell,[31] but the work reported during the past twelve months has not forced acceptance of such a production upon the sceptical. As J. Needham [32] points out in dealing with oxygen consumption without carbon dioxide production in acidified hen or crab eggs, such a phenomenon may be due to a variety of causes other than the production of sugar or keto-acids from fats; *e.g.*, oxidation of sulphur to sulphate, of lactic acid to pyruvic acid, of glucose to glycuronic acid. It is, however, doubtful whether these, in man, are of sufficient quantitative importance to account for the low values of the R.Q. which have been recorded.

Heavy Water.

The biological behaviour of D_2O is receiving attention, though, naturally, not a great deal of progress has yet been made. Nevertheless, a number of short papers have appeared which combine to give the impression that living cells are by no means indifferent to the proportions of H_2O and D_2O in the surrounding media, and that a normal concentration of heavy water may be essential to the processes of life.

The fact that pure D_2O is definitely toxic and kills certain small organisms at a rate generally proportional to their degree of complexity was reported last year.[33] G. N. Lewis,[34] however, states that the toxicity is not very great to such varied organisms as tobacco seeds, yeast, flatworms, and mice; and lower organisms tolerate it in high concentrations. He finds that the rate of the vital processes is roughly inversely proportional to the concentration of D_2O, and that in pure D_2O growth is extremely slow if it takes place at all.

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[28] E. E. Hawley, C. W. Johnston, and J. R. Murlin, *Amer. J. Physiol.* 1933, **105**, (Proc.) 46; *A.*, 1934, 441; *J. Nutrition*, 1933, **6**, 523; *A.*, 1934, 320.

[29] *J. Clin. Invest.*, 1933, **12**, 968.

[30] *J. Physiol.*, 1933, **79**, 508; *A.*, 1934, 683.

[31] *J. Nutrition*, 1933, **6**, 473.

[32] *Proc. Soc. Exp. Biol. Med.*, 1932, **30**, 182; *A.*, 1933, 1324.

Even low concentrations of heavy water have a definite effect on cellular metabolism and on enzyme systems. T. C. Barnes[35] found that in water of *d* 1·000061, filaments of *Spirogyra nitida* were characterised by lack of movement, absence of abscission or cell disjunction, and greater longevity. Later,[36] he reported that in heavy water (*d* 1·000061) a filament of 31 cells of *Spirogyra nitida* had increased to 43 cells (3 dead) after six days, whereas in ordinary water under similar conditions no cell division had taken place, in ice-water there were 15 abnormal cells out of 50 after five days, and in freshly condensed water all the cells died. Similarly he[37] found cells of *E. gracilis* to multiply more rapidly in water containing a low percentage of D_2O than in ordinary distilled water, and a stimulating effect of D_2O (in small concentrations) on the vegetative growth and development of *Aspergillus* sp. has been reported by S. L. Meyer.[38]

Dealing with enzyme systems, Barnes and Larson found that heavy water (*d* 1·000061) decreased the rate of starch hydrolysis by pancreatic amylase, and the amount of carbon dioxide evolved during zymase fermentation. On the other hand, oxidation of guaiaconic acid by a peroxidase–oxygenase system was increased by making the solution in ice-water and allowing it to warm to room temperature.

H. Erlenmeyer and H. Gärtner[39] find that, within experimental error, the animal body does not change the D_2O content of water, since 8 litres of pure water yielded 20 c.c. of heavy water of *d* 1·00087, and cow's milk similarly treated gave water of *d* 1·00083. This is, of course, an important observation for those workers who use heavy water as an indicator of water movement in the animal body. This has been done in the case of fish (goldfish), in which it appears that nearly all the water leaves the body and is replaced by fresh within a few hours,[40] and in man, where the exchange takes many days. In man, G. von Hevesy and E. Hofer [41] found that half the ingested heavy water was excreted in 9 (± 1) days, and calculated the average "life" of a water molecule within the body to be 13 (± 1·5) days. Their calculations involved the assumption that the ingested water was completely mixed with the water present in the body, and this assumption has been verified by H. Erlenmeyer *et al.*[42] These workers found that injection of isotonic heavy water (1·64%) solutions of xylose into jejunal loops of rats led to reduction of the heavy water content to 0·05—0·07% without diminution of the total volume. Calculation showed that this meant the distribution of the heavy water over 127—135 c.c., the total water content of the body being 132 c.c. The absorption was very rapid, the figures quoted being obtained in one hour.

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[33] *Ann. Reports*, 1933, **30**, 34.

[34] *Science*, 1934, **79**, 153; *A.*, 557.

[35] *J. Amer. Chem. Soc.*, 1933, **55**, 4332; *A.*, 1933, 1329.

[36] T. C. Barnes and E. J. Larson, *ibid.*, p. 5059; *A.*, 1934, 217.

[37] *Science*, 1934, **79**, 370; *A.*, 692.

[38] *Ibid.*, p. 210; *A.*, 562.

[39] *Helv. Chim. Acta*, 1934, **17**, 334; *A.*, 546.

PLANT BIOCHEMISTRY.

Fixation of Nitrogen by Nodule Bacteria.

Investigations of the symbiotic relationships between leguminous plants and *Rhizobia*, culminating in recent years in the development of practical methods of field inoculation, have brought in their train a much wider knowledge of the nutrition and metabolism of these bacteria. Contrary to earlier views, it is now firmly established that the nodule bacteria are unable to fix nitrogen in the absence of the host plant.[1, 2, 3] Moreover, the organism, previously supposed to be strictly aërobic, has been shown to maintain its activity under anaërobic conditions in the presence of a hydrogen-acceptor. Its growth in nodules in which the oxygen supply is, to say the least, much restricted, now receives adequate explanation.

The general association of rapid vegetative growth in legumes with extensive nodule formation in the roots has led to many investigations of the balance between the ability of the plant to supply carbonaceous energy material to the nodule bacteria and that of the bacteria to provide assimilable nitrogen for the plant. In this connexion, P. W. Wilson and colleagues[4, 5, 6] have examined the frequently observed beneficial effect of an artificially increased proportion of atmospheric carbon dioxide on the growth and nodulation of legumes. With *Rh. trifolium* it is shown that in a normal atmosphere the rate of carbon assimilation by red clover, rather than that of nitrogen fixation by the bacteria, is the limiting factor in this symbiotic system. With a carbon dioxide content of approximately 0·3%, carbon assimilation reaches an intensity sufficient to meet the energy requirement of the nodule organisms for maximum fixation of nitrogen. The critical carbon dioxide content for balanced conditions depends on external conditions, notably those controlling the difference between the intake and respiration of carbon dioxide, and the rate and extent to which carbon dioxide liberated by the bacteria can diffuse through the growth medium and again become utilisable by the leaves. Increased assimilation results not only in an increasing growth and nitrogen content of the plant and a greater number of nodules, but in enlargement of the nodules and a tendency for their normal distribution round the crown of the roots to be extended to lateral roots.

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[40] G. von Hevesy and E. Hofer, *Nature*, 1934, **133**, 495; *A.*, 557.

[41] *Ibid.*, 1934, **134**, 879.

[42] H. Erlenmeyer, H. Gärtner, E. J. MacDougall, and F. Verzár, *ibid.*, p. 1006.

[1] P. W. Wilson, E. W. Hopkins, and E. B. Fred, *Arch. Mikrobiol.*, 1932, **3**, 322; *A.*, 1932, 549.

[2] F. E. Allison, *J. Agric. Res.*, 1929, **39**, 893; *B.*, 1930, 258.

[3] M. P. Löhnis, *Soil Sci.*, 1930, **29**, 37.

[4] P. W. Wilson, E. B. Fred, and M. R. Salmon, *ibid.*, 1933, **35**, 145; *B.*, 1933, 323.

[5] P. W. Wilson, P. Wenck, and W. H. Peterson, *ibid.*, p. 123; *B.*, 1933, 323.

[6] P. W. Wilson and E. B. Fred, *J. Bact.*, 1933, **25**, 54; *A.*, 1933, 647.

By increasing the pressure of carbon dioxide around sand-cultured plants, C. E. Georgi, F. S. Orcutt, and P. W. Wilson [7] find that all the above effects are accentuated even if the total amount of carbon dioxide to which the plant has access remains unchanged. The production of similar effects by the addition of sucrose or glucose to culture media is attributable to the utilisation of the sugars by the bacteria and to increased carbon assimilation of the plant following the production of carbon dioxide by the organisms. Mannitol produces no such effects and even in moderate concentrations depresses nitrogen fixation. In an examination of soya bean organisms, F. Allam [8] calculates that approximately 15 g. of dry matter from the plant are consumed during the fixation of 1 g. of nitrogen. More recently E. B. Fred and P. W. Wilson [9] confirm the direct relationship between the carbohydrate content of clover and the number of nodules formed, and further show that excessive amounts of sugars in the early stages of growth may cause a temporarily delayed fixation of nitrogen.

A reduced supply of carbohydrate, *e.g.*, when plants are kept in darkness, checks fixation by the bacteria, which then attack the cellulosic matter of the plant tissues.[10] Sugar metabolism in *Rhizobia* takes the form of a butyric fermentation with the production of the customary proportions of carbon dioxide and hydrogen and small amounts of alcohol and acetic acid.[11]

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[7] *Soil Sci.*, 1933, **36**, 375; *B.*, 1934, 114.

[8] *Z. Pflanz. Düng.*, 1931, **20**, *A*, 270; *A.*, 1931, 876.

[9] *Proc. Nat. Acad. Sci.*, 1934, **20**, 403; *A.*, 1273.

[10] H. G. Thornton, *Proc. Roy. Soc.*, 1930, *B*, **106**, 110.

By providing an alternative source of nitrogen to clover, E. W. Hopkins and E. B. Fred [12] find that the size of root nodules is decreased to extents which vary with the nature of the material used, but, in general, vary inversely with concentration of the nitrogen source (potassium nitrate, ammonium sulphate, urea, asparagine, and yeast extract are examined). Under these conditions nodules are found principally on lateral roots. In the presence of mannitol and either nitrogenous substance nodulation is largely confined to tap roots.

The high specificity of the various species of *Rhizobium* in respect of the host plant, sufficiently accentuated to permit the use of agglutination and complement-fixation tests for classification purposes,[13] is reflected, to some extent, in their response to different forms of fixed nitrogen. Thus R. H. Walker and D. A. Anderson [14, 15] record that the oxygen consumption of cultures of four different species is uniformly low in nitrogen-free media, but is increased, by additions of yeast extract, in proportion to the amount of nitrogen thus added. The effect is maintained until the supply of nitrogen is exhausted. If, however, nitrogen is added to cultures of *Rh. leguminosarum*, *Rh. trifolii*, or *Rh. phaseoli* in the form of sodium nitrate or alanine, there is only a small upward trend in oxygen consumption. With ammonium chloride or urea, small concentrations produced little or no effect and larger amounts had a depressive action. The growth and activity of *Rh. meliloti* were definitely increased by all forms of nitrogen examined, the action of urea being intermediate between that of yeast (high) and that of the remaining three simpler compounds, which produced generally similar effects. Characteristic physiological differences between *Rh. meliloti* and other species are shown by A. W. Hofer and I. L. Baldwin [16] to develop in media rich in nitrogen. The decomposition of various nitrogenous compounds by different nodule organisms is also examined by G. G. Pohlman; [17] *Rh. meliloti* produces ammonia from glycine, *dl*-amino-*n*-butyric acid, *dl*-alanine, asparagine, and urea, whereas *Rh. japonicum* acts only on the last three substances named. Differences in the utilisation, without ammonia formation of the amino-groups in glycine, *l*-tyrosine, *dl*-amino-*n*-butyric acid, and urea are also shown by these two species. It is not yet clear, however, to what extent these differences are characteristic of species. In some cases, various strains of the same species appear to vary in their action on nitrogen compounds.

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[11] A. I. Virtanen, M. Nordlund, and E. Hollo, *Biochem. J.*, 1934, **28**, 796; *A.*, 928; *Suomen Kem.*, 1933, **6**, *B*, 62; *A.*, 1933, 752.

[12] *Plant Physiol.*, 1933, **8**, 141; *A.*, 1933, 647.

[13] W. R. Carroll, *Soil Sci.*, 1934, **37**, 117, 227; *A.*, 453; *B.*, 468.

[14] *J. Bact.*, 1933, **25**, 53; *A.*, 1933, 638.

[15] With P. E. Brown, *Soil Sci.*, 1934, **37**, 387; *A.*, 811; *ibid.*, 1934, **38**, 207; *A.*, 1265.

[16] *J. Bact.*, 1932, **23**, 65; *A.*, 1932, 1066.

[17] *Soil Sci.*, 1931, **31**, 385; *A.*, 1931, 876.

The diffusion of bacterial nitrogen from nodules into the surrounding soil and its ultimate utilisation by other plant species are matters of obvious practical importance. The implied breakdown of the bacterial cell is variously ascribed to the action of plant enzymes or to the presence of a specific bacteriophage within the root. According to A. I. Virtanen and S. von Hausen,[18] the diffused nitrogen is almost entirely in the form of amino-acids, which are effective sources of nitrogen for *Gramineae.* In mixed crops of peas and oats, the latter obtained additional nitrogen if the proportion peas : oats was between 1 : 1 and 1 : 2. With smaller proportions of peas, the growth of both crops was depressed.[19] H. G. Thornton and H. Nicol [20] show a similar utilisation of nodule-nitrogen to occur in rye grass when grown simultaneously with lucerne.

Biochemistry of the Higher Plants.

Nitrogen Nutrition and Metabolism.—The great practical and academic interest in the nitrogen relationships of plants is reflected again this year in a heavy output of research work on this subject. The relative efficiency of nitrates and ammonium salts in plant nutrition continues to form the basis of many investigations in which the varying aspects of this intricate problem are being steadily elucidated.

Continuing earlier work,[21] Shive and his colleagues [22] show that ammonia intake by the tomato, as by other plants, is most rapid from neutral or alkaline media, and that of nitrate from acid media. In older plants, however, the absorption of nitrates becomes less affected by p_H, and, in the range p_H 4·0—7·0, usually exceeds that of ammonia at any given p_H. Further, the rate of absorption of ammonia per gram of dry matter in the plant decreases, whereas that of nitrate increases with advancing plant growth. In ammonium nitrate-fed plants the proportion of ammonia in roots increases with the p_H of the medium, and the simultaneous appearance of large amounts of basic-free amino-nitrogen indicates rapid transition of ammonium- to amino-nitrogen within the root system. This is confirmed by the relatively small effects of changes in the rate of ammonia absorption on the ammonia contents of leaves. In these experiments, also, the nitrate content of roots, stems, and leaves was but little changed as a result of variations of p_H and of nitrate intake. It would appear, therefore, that conditions favouring the intake of ammonia or nitrate are also those favouring the assimilation of the respective nitrogen sources. The high proportion of nitrate in stems as compared with roots or leaves of tomato is typical also of a number of other plants.[23] In a somewhat similar investigation of sand-cultured peach trees O. W. Davidson and J. W. Shive[24] show that optimum utilisation of ammonium salts occurs with media of p_H 6·0, whereas that of nitrate shows two optima, at p_H 4·0 and 8·0. Here again the early stages of ammonia assimilation occur in the roots, in which also the reduction of nitrate is practically completed. V. A. Tiedjens,[25] working with tomato and with apple, confirms many of the observations of Shive and also shows that ammonia-fed plants contain more soluble organic nitrogen than those receiving equivalent proportions of nitrate. High proportions of soluble carbohydrates apparently favour ammonium-assimilation.

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[18] *Z. Pflanz. Düng.*, 1931, **21**, *A*, 57; *A.*, 1931, 1101; *Suomen Kem.*, 1933, **6**, *B*, 55; *B.*, 1933, 243; (with H. Karström), *Biochem. Z.*, 1933, **258**, 106; *A.*, 1933, 437.

[19] U. Wartiovaara, *Z. Pflanz. Düng.*, 1933, **31**, *A*, 353; *A.*, 1933, 1092.

[20] *J. Agric. Sci.*, 1934, **24**, 269; *B.*, 550.

[21] *Ann. Reports*, 1933, **30**, 320.

[22] H. E. Clark and J. W. Shive, *Soil Sci.*, 1934, **37**, 203, 459; *B.*, 468, 776.

A comparison of the relative effects of different nitrogen sources on soil cultures of a number of farm crops is recorded by K. Nehring.[26] With acid-sensitive plants, *e.g.*, mustard, ammonium sulphate produces better growth than nitrates at all ranges of p_H examined. A slight advantage is shown by ammonia in alkaline and by nitrate in acid conditions for the development of barley, wheat, and maize. At neutrality no differences are apparent. The nitrogen intake from the various sources, by acid-tolerant plants (oats, rye), is not greatly affected by p_H, and although differences in the growth of ammonia-fed and nitrate-fed plants are small, the latter contain relatively larger proportions of amides as compared with proteins.

An interesting paper by J. P. Conrad[27] records changes in the reaction of media as a result of the growth in them of maize and sorghum plants. The residual (titratable) acidity of cultures containing ammonium sulphate, after absorption of the nitrogen by plants, is greater than that in corresponding media containing sulphuric acid, and the alkalinity of sodium nitrate cultures is less than that of sodium bicarbonate cultures. The residual values for nitric acid, ammonium nitrate, and ammonium carbonate media are all practically the same as when water alone is used. These results are attributed to the necessity of the plant to utilise hydroxyl ions during the assimilation of ammonia, and hydrogen ions for assimilating nitrates. It is suggested that the energy utilised in the absorption of the hydroxyl or hydrogen ions is a factor controlling the effect of p_H on the proportional absorption of nitrate and ammonium salts. D. Prianischnikov[27a] shows that ammonium nitrate in nutrient media may exert a physiologically acid or alkaline reaction in accordance with the age of the plants and the concentration of the nutrient. Under conditions of excessive alkalinity, absorbed ammonia may be re-excreted into the medium. The physiological reaction of ammonium nitrate is also influenced by temperature, since nitrate absorption increases with rising temperature, whereas that of ammonium is unaffected.[28]

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[23] E. Parisi and G. de Voto, *Atti R. Accad. Lincei*, 1932, **16**, 270; *A.*, 1933, 197.

[24] *Soil Sci.*, 1934, **37**, 357; *A.*, 821.

[25] *Plant Physiol.*, 1934, **9**, 31; *A.*, 821.

[26] *Landw. Jahrb.*, 1934, **79**, 481; *B.*, 728.

[27] *J. Amer. Soc. Agron.*, 1934, **26**, 364; *A.*, 1048.

Temperature effects on the nitrogen nutrition of apple are examined by G. T. Nightingale.[29] Simple protein synthesis occurs in the fibrous roots of trees grown in darkness, in sand cultures at 9°, nitrogen being supplied as ammonium sulphate at p_H 6·0 or sodium nitrate at p_H 4·5. Formation of amino-acids and asparagine and the utilisation of carbohydrate proceed more rapidly in the ammonia-fed plants. Protein formed at this temperature, however, remains in the roots, which develop rapidly. By increasing the temperature to 21°, translocation of amino-acids to buds begins and these organs develop rapidly. The reaction of the internal root tissues is unaffected by that of the nutrient media or the nature of the source of nitrogen. In several leguminous plants examined by L. Burkhart[30] the absorption of ammonium salts appears to be influenced to a considerable extent by the nature of the non-nitrogenous plant reserves. Ammonia injury in these plants results from interference with the normal process of utilisation of protein and non-protein reserve substances, and is associated with low proportions of reducing sugars. Amide detoxication is only moderately effective in reducing injury. The ammonia nutrition of rice varies with the nature of the associated anion, absorption decreasing in the order sulphate, phosphate, nitrate, chloride. The differences persist throughout growth except in the case of the nitrate, the ammonia of which is relatively better assimilated in older plants.[31] Sugar cane plants supplied with ammonium salts are observed by G. B. Ulvin [32] to produce less chlorophyll than those receiving nitrate.

[27a] *Z. Pflanz. Düng.*, 1934, *A*, **33**, 134; *B.*, 417.

[28] P. Strebeyko, *Polish Agric. Forestal Ann.*, 1932, **28**, 357; *A.*, 1934, 821.

[29] *Bot. Gaz.*, 1934, **95**, 437; *A.*, 1044.

[30] *Plant Physiol.*, 1934, **9**, 351; *A.*, 1273.

Carbohydrates in Plants.—Starch formation in sugar cane leaves has been further examined by W. M. Coelingh and V. J. Koningsberger.[33] Normally, starch accumulates only in the bundle sheaths. The process continues in darkness if excised leaves are placed in solutions of maltose, sucrose, glucose, or fructose, but starch production is localised in the palisade cells of the parenchyma. Light is required for the translocation of starch to the bundle sheaths. The extent to which these processes occur differs somewhat with the variety of cane examined. During the growth of the cane seasonal variations in total solids and non-reducing sugars in the sap are of a similar character, whereas reducing sugars vary in an inverse direction. In cooler periods sucrose accumulates in stems and may be utilised during the sprouting of stem cuttings, during tasselling and side-shoot formation, or in the renewal of denuded leaves. During such periods the proportion of reducing sugar in saps undergoes little change.[34]

In an interesting investigation of the distribution of carbohydrates and other constituents of the cotton plant, T. G. Mason and colleagues [35, 36] examine the concentration gradients of sugars in various organs under different growth conditions. In addition to sucrose, glucose, and fructose a water-soluble polyglucoside occurs in leaves. Translocation of carbohydrate to the bundles occurs in the form of sucrose. Stored polysaccharides are located chiefly in the bark.

In the examination of carbohydrate changes in plants the practice is frequently adopted of comparing analytical values on a total-dry-weight basis. F. E. Denny [37] indicates that this may sometimes lead to quantitative or even qualitative error and advises the calculation of data in terms of " residual dry weight," *i.e.*, total dry weight *minus* carbohydrates.

The significance of sugar accumulation in vines is examined by L. Moreau and E. Vinet,[38] who show that the rapidly increasing amount of sugar appearing in the fruit during ripening is obtained very largely from the carbohydrate reserves of the main stem. Moreover, sugar accumulation in the sap is a controlling factor in the development of new fruit buds. Variation in the carbohydrate content of roots is discussed by A. C. Arny [39] from the practical viewpoint of the importance of timing cutting operations in weed eradication.

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[31] R. H. Dastur and T. J. Malkani, *Indian J. Agric. Sci.*, 1933, **3**, 157; *B.*, 1934, 33.

[32] *Plant Physiol.*, 1934, **9**, 59; *A.*, 818.

[33] *Arch. Suikerind. Ned.-Indië*, 1932, 1325; *A.*, 1934, 464.

[34] S. Komatsu, S. Ozawa, and Y. Makino, *Mem. Coll. Sci. Kyoto*, 1933, *A*, **16**, 1; *A.*, 1933, 873.

[35] E. Phillis and T. G. Mason, *Ann. Bot.*, 1933, **47**, 585; *A.*, 1933, 988.

[36] T. G. Mason and E. J. Maskell, *ibid.*, 1934, **48**, 119; *A.*, 335.

[37] *Contr. Boyce Thompson Inst.*, 1933, **5**, 181; *A.*, 1933, 873.

[38] *Ann. agron.*, 1932, **3**, 363; *A.*, 1933, 102.

The effect of disease on carbohydrate variations in plants forms the subject of numerous investigations. Leaf-roll in potato disturbs the normal translocation of sucrose as a result of damaged phloem, and although there is some passage of hexose through the parenchyma, starch steadily accumulates in leaf laminæ.[40] Tobacco virus brings a decline in leaf carbohydrate,[41] differences from normal being especially marked in periods of active photosynthesis. During the storage of healthy leaves there is a steady decrease in insoluble carbohydrates, whereas in diseased leaves the loss falls principally on the disaccharide fraction.[42]

Rust in wheat causes a reduction in the percentage of sucrose and an increase in that of starch in the grain, although the total starch per grain is subnormal.[43]

Other observations of this character include the occurrence of a general increase in reducing sugars, sucrose, starch, and polysaccharides in the leaves of lucerne and clover following injury by the leaf hopper;[44] a partial replacement of carbohydrate by pentosans and galactan in rutabagas exhibiting " dark centre "; and the association of " blind wood " in roses with abnormally high accumulation of insoluble carbohydrates in stems and leaves, as compared with the flowering shoots which contain large proportions of reducing sugars.

Glucosides.—Seasonable variations in cyanogenetic-glucoside content of *Sorghum vulgare* are recorded by C. N. Acharya.[45] Maximum yields of hydrocyanic acid were obtained from very young plants or young, actively growing side shoots of older stocks. The proportion declined with advancing age to a minimum at the flowering stage. Cyanogenetic material accumulates chiefly in leaves and the yield is the same whether seedlings are grown in darkness or in daylight. Daily variations show minima in early morning and evening and a maximum soon after mid-day. In the preparation of material for analysis, treatment with chloroform or toluene does not check the enzymic liberation of hydrocyanic acid. The possibility of the presence in *Sorghum* of cyano-compounds other than glucosides is indicated. A daily periodicity in the glucoside content of *Aesculus* leaves is reported G. Kerstan,[46] who makes the interesting observation that æsculin in the bark of twigs is not easily translocated and does not function as a carbohydrate reserve. In leaves, however, æsculin is mobile. An unusual practical application of glucoside analysis is indicated by an examination of New Zealand clovers. It is shown that the amount of hydrocyanic acid obtainable from individual types, although subject to seasonal variations, falls within limits sufficiently narrow to permit differentiation among different types.[47, 48] H. O. Askew [49] also describes a satisfactory method for the preparation and analysis of the material.

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[39] *Minnesota Agric. Exp. Sta. Tech. Bull.*, 1932, No. 84; *A.*, 1933, 328.

[40] E. Barton-Wright and A. McBain, *Trans. Roy. Soc. Edin.*, 1932, **57**, 309; *A.*, 1933, 546.

[41] J. Caldwell, *Ann. Appl. Biol.*, 1934, **21**, 191, 206; *A.*, 1030.

[42] H. Cordingley, J. Grainger, W. H. Pearsall, and A. Wright, *ibid.*, p. 78; *A.*, 466.

[43] R. M. Caldwell, H. R. Kraybill, J. T. Sullivan, and L. E. Compton, *J. Agric. Res.*, 1934, **48**, 1049; *B.*, 978.

[44] H. W. Johnson, *Phytopath.*, 1933, **23**, 19; *B.*, 1933, 565; E. B. Holland and C. P. Jones, *J. Agric. Res.*, 1934, **48**, 377; *A.*, 822.

[45] *Indian J. Agric. Sci.*, 1934, **3**, 851; *A.*, 710.

Among new examinations of glucosides in plants may be mentioned those of H. Colin and A. Chadun,[50] who isolate a fructoside from *Scilla*, of G. Tanret [51] on the nature of coronillin from *Coronilla* seeds, the preparation of kæmpferol rhamnoside from leaves of *Pueraria hirsuta*,[52] and a further examination of salireposide [53] by M. Wattiez,[54] who now describes this substance as a benzoate of a heteroside yielding β-glucose on hydrolysis.

Mineral Nutrition.—Potassium. That the efficiency of potassium in plant nutrition is influenced by the nature of associated cations has long been recognised. E. Blanck and W. Heukeshoven [55] make the rather unexpected observation that the yield response of beans to potassium is higher for the oxalate, citrate, and formate than for the sulphate. Moreover, the anionic influence shows itself not only in affecting the total intake of calcium, phosphorus, and nitrogen, but also in the distribution of these elements between seed and straw. This is perhaps related to the fact that the utilisation of calcium phosphate by plants to which the various salts were applied is paralleled by the solubility of calcium phosphate in the respective salt solutions. In an examination of the distribution of potassium in potato plants W. O. James and N. L. Penston [56] indicate a continuous circulation of potassium in the plant in the form of salts of amino-acids. Deficiency of potassium lowers the activity of enzymes in plants and also the relative order of activity in various plant organs. Thus M. Cattle [57] establishes that lowered diastatic activity is more pronounced in young and in old leaves than in those of intermediate age. Similarly, invertase activity in upper leaves is diminished and that of lower leaves increased by potassium starvation. The decline in invertase activity has also been observed in sugar cane by C. E. Hartt.[58] The well-known relationships between the formation of carbohydrates in plants and the supply of potassium suggest that light intensity may exert a controlling influence in potassium nutrition. K. Scharrer and W. Schropp,[59] working with peas, show an inverse relationship between the optimum potassium requirement and the period of exposure of the plants to light. Impoverished growth due to deficiency of light is to a considerable extent counteracted by increased feeding with potassium. Similar conclusions are reached by R. Schwartz [60] in the course of field manurial trials of the effect of potash fertilisers on the seed yield of *Lolium italicum.*

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[46] *Planta*, 1934, **21**, 676; *A.*, 1048.

[47] B. W. Doak, *New Zealand J. Sci. Tech.*, 1933, **14**, 359; *B.*, 1933, 839.

[48] T. Rigg, H. O. Askew, and E. B. Kidson, *ibid.*, 1933, **15**, 222; *A.*, 1934, 229.

[49] *Ibid.*, p. 227; *A.*, 229.

[50] *Bull. Soc. Chim. biol.*, 1933, **15**, 1520; *A.*, 1934, 464.

[51] *Compt. rend.*, 1934, **198**, 1637; *A.*, 709.

[52] T. Ohira, *J. Agric. Chem. Soc. Japan*, 1933, **9**, 337; *A.*, 1933, 1216.

[53] *Ann. Reports*, 1931, **28**, 244.

[54] *Bull. Acad. roy. méd. Belge*, 1932, **12**, 433; *A.*, 1934, 1276.

[55] *J. Landw.*, 1933, **81**, 291.

Iron and manganese and their relation to chlorosis. The appearance of chlorosis in plants is frequently traced to deficiencies within the plant of iron or manganese and since the solubility of many soil minerals containing these elements is lowered by reaction changes towards alkalinity, the explanation of lime-induced chlorosis seemed a simple one. Recent investigations indicate that other factors are concerned. The intake of manganese [61, 62] and iron [63] by plants is conditioned by the nature of the compounds concerned and by the presence of other substances. Thus the absorption of manganese from the dioxide by wheat seedlings is depressed by additions to nutrient media of sodium nitrate and calcium carbonate. No depression occurs when manganese chloride is used. The reduced intake caused by additions of phosphate is especially marked

[56] *Ann. Bot.*, 1933, **47**, 279; *A.*, 1933, 649.
[57] *New Phytol.*, 1933, **32**, 364; *A.*, 1934, 337.
[58] *Hawaiian Planters Rec.*, 1933, **37**, 13; *B.*, 1934, 340.
[59] *Z. Pflanz. Düng.*, 1934, *A*, **35**, 185; *B.*, 1075.
[60] *Ernähr. Pflanze*, 1934, **30**, 293; *B.*, 1027.
[61] J. Davidson, *Proc. 2nd Internat. Cong. Soil Sci.*, 1933, II, 84; *A.*, 1934, 337.
[62] C. Olsen, *Compt. rend. Trav. Lab. Carlsberg*, 1934, **20**, No. 2; *A.*, 1048.
[63] W. Schropp, *Z. Pflanz. Düng.*, 1934, *A*, **33**, 38; *B.*, 340.

in the case of manganese chloride and sulphate. Similar influence of anions on the absorption of iron by plants is also described. The availability to plants of organic compounds of iron is found to be much less affected by reaction changes than that of many inorganic forms.

Extensive investigations in Germany[64, 65, 66] of chlorosis in the yellow lupin indicate that the effect of lime is not limited to restricting the intake of iron by plants, but extends within the plant system itself, where the iron is rendered immobile in the older leaves. Young leaves become chlorotic even when the total amount of iron within the plants may be sufficient to meet their requirements. In the case of the blue lupin iron deficiency is related to the presence of manganese, which is an essential nutrient for this plant. W. Scholz[67] shows that excessive proportions of manganese in the blue lupin plant produce no injury provided a sufficiency of iron is present. If the iron supply is restricted, as in lime-chlorosis, manganese intensifies the injury. Deficiency of manganese in the plant, however, may cause a characteristic manganese-chlorosis distinct from that resulting from shortage of iron. Lime-induced chlorosis is also observed in flax,[68] and in this case also, the customary treatment of the soil with iron salts is rendered inoperative if much manganese is present in the plant.

A magnesium-chlorosis may occur as the result of excessive applications of magnesium carbonate to soils.[69] It resembles lime-chlorosis in being associated with iron deficiency in leaves, and in its response to additions of iron salts to soil.

Copper. F. G. Anderson[70] cites a case of chlorosis due to copper deficiency in leaves, remedied by spraying with copper sulphate solution, and B. D. Wilson and G. R. Townsend[71] record the remarkably improved productivity of peat soils following treatment with copper sulphate. Similar effects were obtained by R. V. Allison[72] and co-workers, in the saw-grass peats of Florida. It is suggested in this case that in addition to its nutritional function, copper protects the root surface from injury by toxic organic

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[64] R. Reincke, *Z. Pflanz. Düng.*, 1931, *A*, **23**, 77; *B.*, 1932, 125.

[65] W. Scholz, *ibid.*, 1932, *A*, **25**, 287; 1933, *A*, **28**, 257; *A*, **29**, 59; 1934, *A*, **33**, 340; *B.*, 1932, 907; 1933, 567, 599; 1934, 517.

[66] S. Triwosch, *ibid.*, 1933, *A*, **31**, 14; *B.*, 1933, 884.

[67] *Ibid.*, 1934, *A*, **35**, 88; *B.*, 937.

[68] W. Scholz, *ibid.*, 1934, *A*, **34**, 296; *B.*, 901.

[69] S. Triwosch, *ibid.*, 1934, *B*, **13**, 155; *B.*, 597.

[70] *J. Pomology*, 1932, **10**, 130; *B.*, 1932, 907.

[71] *J. Amer. Soc. Agron.*, 1933, **25**, 523; *B.*, 1933, 1073.

[72] *Proc. 4th Cong. Int. Soc. Sugar Cane Tech. Bull.*, 1932, No. 112; *B.*, 1933, 759; *Proc. 2nd Interat. Cong. Soil Sci.*, 1930, VI, 257; *B.*, 1933, 243.

substances known to exist in these soils. Deficiency of copper is shown to be the cause of exanthema in pears [73] and of pecan rosette.[74]

Boron. Considerable interest centres on the essential nature of boron for the growth of plants. The actual requirement (and also the minimum lethal dosage) varies considerably with species. Boron-deficiency affects the development of plants in a variety of ways, prominent among which is the curtailment of root growth, *e.g.*, in flax,[75] maize, and potatoes.[76] This effect is probably related to the influence of boron on the calcium-intake of plants. K. Warington [77] shows that the addition of boron to nutrient solutions for *Vicia faba* increases the gross amount of calcium absorbed, and also prolongs the period during which the rate of intake of calcium is increasing. The direct relationship between the amount of calcium absorbed and that supplied is maintained after boron treatment, but the general level of intake is raised. The normal decline in the ratios N/Ca and K/Ca in plants with advancing maturity appears to be accelerated by the presence of boron. Symptoms of boron deficiency appear more slowly in spring and autumn as a result of the shorter period of daylight. Temperature is a less important factor in this respect.[78] The stimulatory action of boron on root growth is shown by its ability to minimise the injury to sugar beet caused by root and crown rots.[79] According to O. Kaufmann,[80] borax is much more efficacious than boric acid for this purpose, and its protective action persists in soil for several years. E. V. Bobko and M. A. Belvoussov [81] record optimum growth of beet in nutrients containing 5 mg. of boric acid per litre. The ill effects of heavy liming on the growth of beet in field soils are counteracted by relatively small dressings of boric acid. In an examination of a boron-deficiency disease of lettuce, J. S. McHargue and R. K. Calfee [82] show that boron may be added to culture media in the form of simple borates (that of manganese avoids toxic effects) or as borosilicate in the form of powdered glass. Boric acid is essential to the development of pollen grains in certain tropical water lilies,[83] and borax is associated with marked stimulatory effect on the yield of beans.[84]

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[73] J. Oserkowsky and H. E. Thomas, *Science*, 1933, **78**, 315; *A.*, 1934, 122.

[74] A. O. Alben, J. R. Cole, and R. D. Lewis, *Phytopath.*, 1932, **22**, 595; *B.*, 1932, 954.

[75] M. Školnik, *Bull. Acad. Sci. U.S.S.R.*, 1933, **7**, 1163; *B.*, 1934, 463; *Compt. rend. Acad. Sci. U.S.S.R.*, 1934, **2**, 104; *B.*, 597.

[76] K. Scharrer and W. Schropp, *Z. Pflanz. Düng.*, 1933, **28**, *A*, 313; *B.*, 1933, 518.

[77] *Ann. Bot.*, 1934, **48**, 743; *A.*, 1274.

[78] K. Warington, *Ann. Bot.*, 1933, **47**, 429; *A.*, 1933, 989.

[79] K. Scharrer and W. Schropp, *Landw. Jahrb.*, 1934, **79**, 977; *B.*, 1026.

[80] *Deut. Zuckerind.*, 1934, **59**, 305; *B.*, 852.

[81] *Ann. agron.*, 1933, **3**, 493; *B.*, 1933, 1073.

[82] *Plant Physiol.*, 1933, **8**, 304; *B.*, 1934, 645.

Plant Growth-promoting Substances (Plant Hormones).

It has long been realised that, although current knowledge affords an explanation in some detail of the chemical mechanism of nutrition, assimilation, metabolism, and synthesis in plants, the manner in which this mechanism is controlled and structural development regulated in response to varied external conditions depends upon characteristically different factors. Indeed it is only during the last few years that the activity of growth-regulating substances, hormones, auximones, etc., has been regarded as possibly due to specific chemical substances. The spectacular work of F. Kögl and his colleagues [85] in elucidating the chemical nature of auxin marks a very important stage of development in the subject and may well form the source of inspiration of an enormous field of investigation for the biochemist.

Auxin-A.*

Many aspects of plant development involve the elongation of individual cells (as distinct from their multiplication), and numerous investigators [86] have indicated that this process is influenced by a hormone-like substance which increases the plasticity of the cell wall and, possibly as a direct result of cell turgidity, thus facilitates elongation.

The active material, auxin (so-named by Kögl),[87] is usually detected and determined by its ability to promote renewed growth of *Avena* coleoptiles following decapitation. In Went's now generally adopted technique, the auxin, prepared in agar, is applied asymmetrically to the cut surface of the coleoptile stump and by causing proportionally greater extension on the treated side, produces a curvature which increases with the potency of the preparation. The cuticle of the coleoptile is not readily permeable to auxin in agar. Auxin readily penetrates the external tissue of roots, however, and here produces a restriction of elongation.

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[83] T. Schmucker, *Naturwiss.*, 1932, **20**, 839; *A.*, 1933, 105.

[84] M. Gorski, *Polish Agric. Forestal Ann.*, 1932, **28**, 27; *B.*, 1934, 597.

[85] *Ann. Reports*, 1933, **30**, 195.

[86] Among others, see F. W. Went, *Rec. Trav. bot. néerl.*, 1928, **25**, 1; A. N. J. Heyn, *ibid.*, 1930, **28**, 113; N. Cholodny, *Biol. Zentr.*, 1927, **47**, 604.

[87] F. Kögl and A. J. Haagen-Smit, *Proc. K. Akad. Wetensch. Amsterdam*, 1931, **34**, 1411; *A.*, 1932, 661.

* In the following pages the word " auxin " refers always to Auxin-*A*. Auxin-*B* is so written in all cases.

Occurrence in Plants.—The rapidly growing apical tissues of roots and shoots of plants contain relatively large accumulations of auxin, and Went [88] originally extracted this by standing freshly cut tips on an agar block, into which a portion of the hormone diffused. Extraction by solvents has now been adopted, auxin being separated in the ether-soluble fraction from various plant organs.

The proportion of auxin in coleoptiles decreases from the tip towards the base [89] and, according to observations of K. Koch,[90] the hormone is concentrated very largely in the 0·2 mm. of the apex. In sections distant more than 3 mm. from the tip, scarcely detectable amounts are found. The growing tips of young plants have more auxin than those of older plants [91] and in *Avena* the amount formed tends to decrease with rising temperature of germination. In apical tissues of seedlings, light influences the production of auxin, and in the case of *Lupinus albus* cited by A. E. Navez [92] approximately twice as much was found in lighted seedlings as in those grown in darkness. Auxin occurs in similar proportions in the tips of both young and old roots of *Zea mais*,[93] but in a number of other species examined, Cholodny (*loc. cit.*) was unable to detect the hormone by the *Avena* method. Cholodny favours the view that auxin is actually formed in the root tip, but doubt on this point is expressed by E. Bünning,[94] C. J. Gorter,[95] K. V. Thimann,[96] and others, who assume the translocation of the substance from aerial parts of the plant.

Cholodny also records a marked decline in the activity of excised root tips after 5—6 hours unless an appropriate nutrient (in this case, gelatin) is provided. This apparent exhaustion of the hormone may also explain the cessation of elongation of sections of *Avena* coleoptiles after immersion in water for a similar period.[97] Under these conditions growth continues on further treatment with auxin.

Pollen Hormone.—F. Laibach and colleagues have made an extensive examination of the growth-promoting substances occurring in the pollen of certain orchids and of *Hibiscus*. Pollen produces the customary effect of auxin on *Avena* coleoptiles,[98] causes enlargement of the gynosternium, accelerates or renews the growth of flowering stems and tendrils, restricts the growth of side-shoots when applied to cut main stems, and stimulates root production on cut stems of a number of plants.[99] The hormonal potency of pollen is very high and is retained for long periods. This is ascribed [1] to the fact that the substance does not occur actually in the pollen grains but in the caudicle, the plastic nature of which affords a protective action. By incorporation of lanolin with pollen extracts Laibach produces a concentrated auxin preparation of persistent activity, which in addition to the ordinary effect on decapitated coleoptiles is capable of producing curvature in intact coleoptiles when painted on one side, and a corresponding (reverse) curvature in similarly treated aerial roots of *Cissus gongyloides.*

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[88] *Loc. cit.* [89] K. V. Thimann, *J. Gen. Physiol.*, 1934, **18**, 23; *A.*, 1272.

[90] *Planta*, 1934, **22**, 190—220; *A.*, 1272.

[91] H. G. van der Wey, *Proc. K. Akad. Wetensch. Amsterdam*, 1931, **34**, 875; *A.*, 1932, 201.

[92] *Proc. Nat. Acad. Sci.*, 1933, **19**, 636; *A.*, 1933, 987.

[93] N. Cholodny, *Planta*, 1934, **21**, 517; *A.*, 1044.

[94] *Planta*, 1927, **5**, 635.

[95] Dissert., Utrecht, 1932. [96] *Loc. cit.*

[97] J. Bonner, *J. Gen. Physiol.*, 1933, **17**, 63; *A.*, 1933, 1214.

[98] *Ber. deut. bot. Ges.*, 1932, **50**, 383; 1933, **51**, 336; *A.*, 1933, 103; 1934, 120.

Occurrence in Fungi, etc.—Auxin was isolated from cultures of *Rhizopus suinus* by N. Nielsen [2] and its properties were studied by H. E. Dolk and K. V. Thimann.[3] According to these authors hormone production is favoured by aeration, is influenced by the state of purity of the peptone used in media, and is paralleled by the formation of carotenoid colouring matter. The occurrence of the hormone is associated with the production of sporangia and is probably concerned in the germination of spores. Nielsen also obtained auxin from *Boletus edulis*, but was unable to detect it in *Psallista campestris.*[4] The production of active material from *Aspergillus niger* has been examined by P. Boysen-Jensen,[5] who regards auxin merely as a metabolic product of the fungus and as playing no part in its growth. Formation in the organism depends on the nature of its nitrogen nutrient. The presence of certain amino-acids of high molecular weight appears necessary. Peptone and hæmoglobin are effective in this respect. Inorganic forms of nitrogen are unsuitable.[6] T. Sakamura and T. Yanagihara [7] confirm the formation of auxin in media containing peptone and also sodium nucleate, but show that alanine, asparagine, aspartic and glutamic acids are ineffective sources of nitrogen. The growth substance is produced in aërobic and in anaërobic cultures. Its formation is inhibited by the presence of glucose (contrary to Boysen-Jensen's observation), sucrose, fructose, maltose, galactose, and glycerol, but not of mannitol or lactose.

[99] F. Laibach, A. Müller, and W. Schäfer, *Naturwiss.*, 1934, **22**, 588; *A.*, 1272. This effect is also produced by Kögl's auxin.

[1] F. Laibach, *Ber. deut. bot. Ges.*, 1933, **51**, 386.

[2] *Jahrb. wiss. Bot.*, 1930, **73**, 125; *Biochem. Z.*, 1931, **23**, 244.

[3] *Proc. Nat. Acad. Sci.*, 1932, **18**, 30, 692; *A.*, 1932, 549; 1933, 327.

[4] *Biochem. Z.*, 1932, **249**, 196; *A.*, 1932, 887.

[5] *Ibid.*, 1932, **250**, 270; *A.*, 1932, 1065.

[6] *Ibid.*, 1931, **239**, 243; *A.*, 1931, 1334.

[7] *Proc. Imp. Acad. Tokyo*, 1932, **8**, 397; *A.*, 1933, 197.

The hormonal preparation from yeast recorded by N. Nielsen [8] also contains auxin, which is presumably the active agent of yeast extracts concerned in stimulating the blossoming of peas.[9]

Various species of bacteria [10] when grown on peptone media produce auxin, which has also been isolated from the marine alga *Valonia macrophysa*, in which it is mainly concentrated in the cell walls.[11]

Occurrence in Animal Organs.—The distribution of auxin is not limited to the plant kingdom. It has been found in the blood, liver, and kidneys of guinea pigs, in rabbit lungs, in pig's thyroid, in human and mouse carcinoma, and in a wide variety of other animal tissues.[12] Much larger proportions were obtained by Kögl and colleagues [13] from urine, the source of the material used in their investigations of the chemical constitution of the hormone. Urinary excretion of auxin seems very largely controlled by the dietary intake and is not influenced by age, sex, pregnancy, or menstruation, or by carcinomatous or tuberculous conditions.[14]

Geotropism, Phototropism, and Electrotropism in Plants as related to Auxin-A.—The relationships between the action of auxin and geotropic and phototropic curvature in plants have provided an interesting field of investigation. F. W. Went (*loc. cit.*) and also E. Seubert [15] have shown that decapitated *Avena* coleoptiles when placed horizontally can be stimulated to further growth with normal geotropic curvature if the hormone is placed symmetrically on the stump. H. E. Dolk [16] assumed that under these conditions auxin was translocated preferentially to the under side of the coleoptile and induced the normal upward curvature. If the auxin is placed asymmetrically on the horizontal stump, geotropic response in the new growth is retarded or enhanced according as the auxin is applied to the upper or the lower side of the stump.[17, 18, 19] In corresponding experiments with roots it has been shown that in these organs also geotropic response is associated with the movement of auxin to the lower side of the tip with consequent restriction of elongation on this side.[20, 21]

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[8] *Biochem. Z.*, 1931, **236**, 205; *A.*, 1931, 1091.

[9] A. I. Virtanen and S. von Hausen, *Nature*, 1933, **132**, 408; 1934, **133**, 383; *A.*, 1933, 1093; 1934, 463; V. Subrahmanyan and G. S. Sidappa, *ibid.*, 1933, **132**, 713; *A.*, 1933, 1342.

[10] P. Boysen-Jensen, *Biochem. Z.*, 1931, **236**, 205; *A.*, 1931, 1091.

[11] H. G. van der Weij, *Proc. K. Akad. Wetensch. Amsterdam*, 1933, **36**, 759; *A.*, 1934, 120.

[12] E. Maschmann, *Naturwiss.*, 1932, **20**, 721; *A.*, 1932, 1156; E. Maschmann and F. Laibach, *ibid.*, 1933, **21**, 517; *A.*, 1933, 1213; F. Kögl, A. J. Haagen-Smit, and B. Tönnis, *Z. physiol. Chem.*, 1933, **220**, 162; *A.*, 1933, 1213.

[13] Summaries of this work are to be found in *Angew. Chem.*, 1933, **46**, 469; *A.*, 1933, 987; *Rep. Brit. Assoc.*, 1933, 600; *Naturwiss.*, 1933, **21**, 17; *A.*, 1933, 435.

[14] F. Kögl, A. J. Haagen-Smit, and H. Erxleben, *Z. physiol. Chem.*, 1933, **220**, 137; *A.*, 1934, 1213.

[15] *Z. Bot.*, 1925, **17**, 49.

[16] *Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 1113; Dissert., Utrecht, 1930.

Similarly the normal phototropic response of a coleoptile which is weakened or eliminated by decapitation is restored by symmetrical placement of auxin in agar on the stump. Asymmetrical application causes a restricted or accentuated response according as activation is on the near or the far side of the stump with respect to lateral illumination. Similar effects are produced by removal of one half of the coleoptile tip (Koch, *loc. cit.*). It is concluded that in the normal coleoptile auxin tends to move towards the shaded portions of the stem.

The conception of the existence of a potential gradient in the plant system, and of its variation with the rate of growth, is of long standing. The known growth response of plants to an artificially applied electric field has been shown by Dolk, Went, Cholodny (*locc. cit.*) and other workers to be explicable by the translocation of auxin within the plant towards positive polarity. Kögl (*loc. cit.*) observed that the potency of his auxin preparation as measured by the *Avena* method varied hourly, and from day to day. He finally traced this effect to variations in the electrical condition of the atmosphere. Further, by passing very small currents through the agar–auxin block and the coleoptile stump on which it was placed, he demonstrated that the curvature per auxin unit could be varied at will by changing the polarity of the system, to accelerate or retard the normal basal movement of the hormone. The acid character of auxin indicates a tendency to migrate towards the positive pole, and Koch [22] explains the electrotropic curvature of stems towards the positive by the impermeability of the cuticle to aqueous solutions. The cuticle acts as an insulating medium, and an externally applied potential difference induces a reversed polarity within the tissue itself. As a result, auxin moves toward the internal positive (*i.e.*, towards the external negative) pole, producing curvature towards the external positive. The view is confirmed by insertion of needle electrodes through the cuticle directly into the tissue; curvature towards the negative pole then occurs. Epidermal tissues

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[17] W. G. du Buy, *Rec. Trav. bot. néerl.*, 1933, **30**, 1.

[18] E. Nuernberk, *Flora*, 1933.

[19] K. Koch, *Planta*, 1934, **22**, 190; *A.*, 1272.

[20] N. Cholodny, *Ber. deut. bot. Ges.*, 1932, **50**, 317; 1933, **51**, 85.

[21] P. Boysen-Jensen, *Planta*, 1933, **20**, 688; *A.*, 1934, 334.

[22] *Loc. cit.*

of roots are freely permeable and no question of induction arises. Curvature is always toward the positive pole.

More recent observations of K. Ramshorn[23] confirm and add detail to earlier records of the electrical conditions obtaining in plants, and demonstrate the electropositive character of zones of rapid growth with respect to the more slowly growing parts.

Tropic movements in general, therefore, are such as to indicate movement of the growth-promoting substance toward the positive pole, towards gravity or away from light and, in general, the effects of artificially applied auxin are superimposed on normal tropic responses.

Cell Extension and Plant Metabolism in Relation to Auxin-A.—Various workers have observed that auxin stimulates cell elongation by increasing the plasticity of the walls. The mechanism by which this is effected would appear to be somewhat complicated. The work of K. V. Thimann and J. Bonner[24] indicates that the action of auxin is not on the formation of cell wall material, nor does it modify the permeability of the wall, but is primarily directed on the protoplasm. They also observe that the respiration of coleoptile sections increases when the proportion of auxin present is small. S. Strugger[25] shows that the growth of seedling shoots of *Helianthus annuus* is stimulated by immersion in acid buffer solutions and that if a longitudinal strip of the epidermis is removed a permanent curvature away from the wound is produced in decapitated (and supposedly auxin-free) hypocotyls. A similar effect is induced in anaërobiosis in which the internal acidity of the cells is automatically increased. Strugger suggests that auxin promotes cell elongation by regulating the course of cell metabolism to produce acid conditions, and in this way influences the rate of growth, which is related to the difference between the p_H and the isoelectric point of the protoplasm.

In a later paper J. Bonner[26] confirms the increased plasticity of cell walls following acid treatment in the case of *Avena* coleoptiles and further shows that the resulting growth increase is inhibited by concentrations of hydrogen cyanide of the same order as those which inhibit the action of auxin. Auxin itself does not increase cell acidity. The stimulative action of acids on decapitated coleoptiles is ascribed to the conversion of inactive salts of auxin remaining in the stump into the active non-dissociated form.

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[23] *Planta*, 1934, **22**, 737.

[24] *Proc. Nat. Acad. Sci.*, 1933, **19**, 714; *A.*, 1933, 1093; *Proc. Roy. Soc.*, 1933, *B*, **113**, 126; *A.*, 1933, 757.

[25] *Ber. deut. bot. Ges.*, 1932, **50**, 77; *A.*, 1933, 102; *ibid.*, 1933, **51**, 193.

[26] *Protoplasma*, 1934, **21**, 406; *A.*, 1272.

The association of geotropic influence with chemical differences in plant tissues is brought out by observations of T. Warner,[27] W. Gundell,[28] and P. Metzner.[29] The undersides of horizontally placed shoots have a markedly increased sugar content and hydrogen-ion concentration, a small increase in catalase activity, and, in the expressed sap, only small differences in osmotic pressure, conductivity, viscosity, and surface tension as compared with the upper sides. In so far as these observations can be interpreted in relation to Strugger's views they are of a confirmatory nature.

Auxin-B.

Associated with auxin-*A* from a number of sources is another growth-substance, differing from it in physiological activity but related to it chemically. The chemical constitution of these substances is more appropriately dealt with in the Organic Chemistry section of these Reports. Apart from physiological distinctions, it is usually sufficient in biochemical work to differentiate between the two substances by the solubility in ether (*A* is soluble) and by resistance to heat and oxidation (*B* is resistant).

Auxin-*B* has no influence on *Avena* coleoptiles, but is usually characterised by accelerating the growth of *Aspergillus niger*. Auxin-*B* occurs with -*A* in *Rhizopus suinus*, in amounts which appear to be related to the p_H of the medium.[30] E. Bünning[31] recently confirmed the presence of auxin-*B* in *A. niger* and examined its action on the growth of the fungus. Auxin-*A* does not affect the weight of mycelium produced or the numbers of conidia, but causes a slightly accelerated formation of conidia and subsequent degeneration. Auxin-*B*, however, produces a very marked increase in mycelium production. Both hormones favour the resorption of nitrate from media and retard that of ammonia. The resulting tendency towards increased p_H in the media may explain the slightly earlier formation of conidia in the presence of auxin-*A*. N. Nielsen and V. Hartelius[32] indicate that auxin-*B* acts on *A. niger* as a result of modification of p_H-growth relationships as in the case of *Rhizopus* (above). Thus optimum growth in the presence of auxin-*B* occurs at p_H 6—7, and in its absence, at p_H 3.

The rate of regeneration of yeast is increased by auxin-*B* to an extent proportional to the amount present. The size of the individual cells is unaffected. Turbidity measurements of yeast cultures are suggested by E. Almoslechner [33] for the quantitative determination of auxin-*B*.

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[27] *Jahrb. wiss. Bot.*, 1928, **68**, 431.

[28] *Ibid.*, 1933, **78**, 623.

[29] *Ber. deut. bot. Ges.*, 1934, **52**, 506.

[30] N. Nielsen and V. Hartelius, *Compt. rend. Trav. Lab. Carlsberg*, 1932, **19**, No. 8; *A.*, 1932, 661.

[31] *Ber. deut. bot. Ges.*, 1934, **52**, 423.

[32] *Compt. rend. Trav. Lab. Carlsberg*, 1933, **19**, No. 15; *A.*, 1933, 1205.

Kögl [34] reports the presence of auxin-*B* in maize oil and in malt. It is also found in *Boletus edulis* and in urine, blood, milk, and a number of vegetables. Examination of preparations from the latter products shows that auxin-*B*, in order to exert its full activity, requires the presence of a complementary substance (" Co-*B* "), which is deficient in a number of the above products. Filter-paper ash and zinc salts appear to fulfil this requirement.[35]

Other Growth-regulating Substances.

Since Wilder first recorded the existence of a growth-regulating substance, " bios," a number of hormone- or vitamin-like substances affecting growth in the plant world have been described. More recently it has been shown that animal hormones and vitamins may also exert a growth-promoting action on plants. Certain similarities in the physiological activities of these substances, or in those of various constituent fractions into which a number of the crude materials have now been resolved, tend towards the view that among plant and animal hormones and vitamins there may well exist closer fundamental relationships than are as yet apparent. This conception is illustrated by such investigations as that of Williams *et al.*[36] Yeast-stimulating preparations, obtained from a wide range of plant and animal products, all contained a polyhydroxylic acid, *panthothenic acid*, very closely related to vitamin-B_2. Wilder's " bios," now shown to contain probably three constituents, induces increased growth in certain fungi. Auxin-*A* preparations from *Avena* and from fungi stimulate yeast growth but do not contain the " Z "-factor regulating fermentation.[37] T. Philipson [38] also records a yeast-stimulating complex in green peas. Two constituents are indicated, neither of which alone shows any activity in this respect. The growth of *Nematospora gossypii*, especially as related to the assimilation of nitrogen compounds, depends on the presence of a growth factor, shown by H. W. Buston and co-workers [39, 40] to be a complex related to "bios," and to contain *i*-inositol as a necessary constituent factor. Among bacteria, *Micrococcus eykmanii* is stimulated by a substance occurring both in plants and in animals, which in some respects resembles but is not identical with auxin. This growth substance depends for its activity on the presence of peptone.[41]

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[33] *Planta*, 1934, **22**, 515.

[34] F. Kögl, H. Erxleben, and A. J. Haagen-Smit, *Z. physiol. Chem.*, 1934, **225**, 215; *A.*, 1044.

[35] V. Hartelius, *Biochem. Z.*, 1933, **261**, 76, 89; *A.*, 1933, 751.

[36] R. J. Williams, C. M. Lyman, G. H. Goodyear, J. H. Truesdail, and D. Holiday, *J. Amer. Chem. Soc.*, 1933, **55**, 2912; *A.*, 1933, 982.

[37] H. von Euler and T. Philipson, *Biochem. Z.*, 1932, **245**, 418; *A.*, 1932, 550.

[38] *Ibid.*, 1933, **258**, 244; *A.*, 1933, 427.

[39] H. W. Buston and B. N. Pramanik, *Biochem. J.*, 1931, **25**, 1656, 1671; *A.*, 1931, 1458.

[40] H. W. Buston and S. Kasinathan, *ibid.*, 1933, **27**, 1859; *A.*, 1934, 230.

Many animal hormones also influence plant growth. For example, W. Schoeller and H. Goebel[42] have demonstrated the action of folliculin in accelerating the development and flowering of hyacinths. Apparently the hormone requires conversion into more readily absorbed sodium salt before becoming effective. Similar results are recorded by M. Janot,[43] who also finds that equilin, equilenin, and dihydrofolliculin are even more active. Injection of thyroid material into bulbs increases the rate of flowering and the number of flowers produced.[44] Thyreoidin stimulates the germination of fungal spores, improves vegetative growth, and accelerates alcoholic fermentation by yeast, but has little influence on bacterial development.[45] The action of thyroxine on plants is mainly directed towards leaf development, whereas adrenaline and hypophysin act principally on roots.[46]

More extensive examinations of the action of vitamin-B on fungi are recorded and serve to illustrate the trend of opinion towards the view that this vitamin has much in common with the typical plant hormones. W. H. Schopfer[47] has prepared from wheat germ, yeast, and pollen a growth substance accelerating vegetative growth and zygote formation in *Phycomyces blakesleeanus*, closely resembling auxin and differing from the vitamin-B complex only in heat resistance and in adsorption by animal charcoal. Vitamin-B_1 and to a lesser extent -B_2 produce similar effects on the fungus, although in this case the action is dependent on the nature of the carbohydrate supply. E. Bünning,[48] working with *A. niger*, shows that vitamin-B_1 has little action on growth except in alkaline media (cf. folliculin, above), whereas -B_2 markedly increases dry matter production. Like auxin-A and -B, the vitamin-B complex favours the absorption of nitrates by the fungus and restricts that of ammonium. Also its action is similarly related to respiratory activity and to reaction changes in the media. W. G. Solheim *et al.*[49] find that vitamins-B_1 and -B_2 stimulate fructification in a number of fungi and increase yellow pigmentation in *A. niger* and *Penicillia*. These physiological similarities among different hormones and vitamins are tending to intensify investigations of the chemical nature of the substances concerned, and provide an enormous stimulus to research in this fascinating branch of biochemistry.

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[41] L. E. den D. de Jong, *Arch. Mikrobiol.*, 1934, **5**, 1; *A.*, 699.

[42] *Biochem. Z.*, 1931, **240**, 1; *A.*, 1931, 1337; *ibid.*, 1932, **251**, 223; *A.*, 1932, 1068; *ibid.*, 1934, **272**, 215; *A.*, 1145.

[43] *Compt. rend.*, 1934, **198**, 1175; *A.*, 463.

[44] E. E. Davies, *Plant Physiol.*, 1934, **9**, 377; *A.*, 1272.

[45] A. A. Imschenetzki, *Bull. Acad. Sci., U.R.S.S.*, 1932, 1559; *A.*, 1933, 868.

[46] D. V. Hykes, *Compt. rend. Soc. Biol.*, 1933, **113**, 629; *A.*, 1934, 934.

[47] *Arch. Sci. phys. nat.*, 1934, [v], **16**, Suppl., 23, 26, 29; *A.*, 1035; *Ber. deut. bot. Ges.*, 1934, **52**, 308.

[48] *Ber. deut. bot. Ges.*, 1934, **52**, 423.

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[49] W. G. Solheim, S. S. Sears, and R. C. Robbins, *Phytopath.*, 1933, **23**, 929; *A.*, 1934, 220.

RADIOACTIVITY AND SUB-ATOMIC PHENOMENA.

In the field of nuclear physics, 1934 has been chiefly notable for two discoveries and for a development in theory which is not unrelated to one of them. The products of artificial disintegration which, hitherto, have always proved to be known or soon-to-be-discovered stable atomic species have now, in a large number of cases, been shown to be unstable and of short life. These "artificial" radio-elements disintegrate with emission of electrons—or in some cases of positrons. They have been produced by bombarding various substances by α-particles, neutrons, protons, and deuterons. Interest in theories of β-disintegration has, very naturally, been increased by this discovery, and two fairly successful theories have been advanced during the course of the year. These have much in common as to their predictions, but show wide differences regarding initial assumptions. The second discovery to which reference has been made is of a nuclear photo-effect. It has been shown that the nuclei of heavy hydrogen and beryllium may be disintegrated by absorption of γ-radiation. In more routine investigations knowledge of the isotopic constitution of many elements has been extended, and several examples of artificial transmutations, previously discovered, have been examined in greater detail. Increased precision has been attained in the measurement of radioactive α-particle and γ-ray energies, under the incentive of theory. The collection of data concerning the penetrating radiation has been carried out as energetically as before, but, at present, no completely satisfactory interpretation appears to have been offered.

The Isotopic Constitution of the Elements.

Masses and Abundance Ratios.—Investigation of the naturally occurring elements by mass-spectrum analysis has been brought one stage nearer a complete first survey by the publication of a series of reports from F. W. Aston.[1] These deal chiefly with the rare-earth elements. At the same time, however, new data have been obtained concerning a number of others. All are included in Table I. Two entries only are derived from other sources, *viz.*, those concerning hydrogen and argon. For argon, P. Zeeman and

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[1] *Nature*, 1933, **132**, 930; 1934, **133**, 327, 684, 869; **134**, 178; *Proc. Roy. Soc.*, 1934, [*A*], **146**, 46; *A.*, 127, 341, 713, 825, 937, 1150.

J. de Gier [2] conclude from positive-ray analysis that A^{38} is present in appreciable amount; the detection of H^3 in naturally occurring hydrogen is the work of W. W. Lozier, P. T. Smith, and W. Bleakney.[3] The new isotope of helium, He^3 (see below), is not included, since it has not as yet been found in any analysis of ordinary helium.

TABLE I.

Element.	At. no.	Mass nos.	Percent. abundance.	Element.	At. no.	Mass nos.	Percent. abundance.
Hydrogen	1	1*	99·99	Neodymium	60	143	11
		2*	0·01			144	30
		3	$<10^{-7}$			145	5
Argon	18	36*	—			146	18
		38		Samarium	62	144	3
		40*				147	17
Calcium	20	40*	96·7			148	14
		42	0·8			149	15
		43	0·2			150	5
		44*	2·3			152	26
Titanium	22	46	f			154	20
		47	f	Europium	63	151	50·6
		48*	s			153	49·4
		49	f	Gadolinium	64	155	21
		50	f			156	23
Nickel	28	56	v.f.			157	17
		58*	—			158	23
		60*	—			160	16
		61	—	Terbium	65	159	—
		62	—	Dysprosium	66	161	22
		64	v.f.			162	25
Zirconium	40	90*	—			163	25
		91	—			164	28
		92*	—	Holmium	67	165	—
		94*	—	Erbium	68	166	36
		96	—			167	24
Rhodium	45	103	—			168	30
Cadmium	48	106	—			170	10
		108	—	Thulium	69	169	—
		110*	—	Yttrium	70	171	9
		111*	—			172	24
		112*	—			173	17
		113*	—			174	38
		114*	—			176	12
		115	—	Lutecium	71	175	—
		116*	—	Hafnium	72	176	f
Lanthanum	57	139*	—			177	s
Cerium	58	140	89			178	s
		142	11			179	s
Praseodymium	59	141*	—			180	s
Neodymium	60	142	36	Thorium	90	232	—

* Indicates a previously-known isotope.

Considered in conjunction with Appendix II of F. W. Aston's "Mass Spectra and Isotopes" (London, 1933), Table I gives the present state of knowledge of the isotopic constitution of the elements.[4]

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[2] *Proc. K. Akad. Wetensch. Amsterdam*, 1934, **37**, 127; *A.*, 578.

[3] *Physical Rev.*, 1934, [ii], **45**, 655.

In the range of mass numbers 1 to 210, only eight are not with certainty allotted to any element, *viz.*, 5, 8, 57, 105, 191, 193, 194, 195. However, analyses of palladium, iridium, platinum, and gold have so far not been effected. When data are available for these elements, it is unlikely that more than four of these gaps will remain.

In Table II the values of atomic weights calculated from masses and abundance ratios, for the rare-earth elements, are compared with the values given in "International Atomic Weights," 1934. The chief discrepancies occur with neodymium and holmium. The calculations from mass-spectrum data are made on the assumption that packing fractions vary regularly from -5×10^{-4} to -3×10^{-4} from the beginning to the end of the rare-earth series. The atomic weight of erbium has recently been determined by O. Hönigschmid and W. Kapfenberger [5] as 165·20. This stands in violent disagreement with the mass-spectrum value and the accepted chemical value. In spite of the apparent consistency of the new chemical analyses, therefore, the Committee of Atomic Weights of the International Union of Chemistry [6] has not at present adopted the lower figure. Eight changes have been made, however, and of these, three, Se 79·2 to 78·96, Te 127·5 to 127·61, Cs 132·81 to 132·91,[7] materially improve the agreement with mass-spectrum values (Se 78·96, Te 127·58, Cs 132·92).[8]

Table II.

	Atomic weight from			Atomic weight from	
Element.	mass-spectrum.	international table.	Element.	mass-spectrum.	international table.
La	138·91±0·05	138·92	Tb	158·91±0·05	159·2
Ce	140·13±0·05	140·13	Dy	162·5 ±0·2	162·46
Pr	140·91±0·05	140·92	Ho	164·91±0·05	163·5
Nd	143·5 ±0·2	144·27	Er	167·15±0·2	167·64
Sm	150·1 ±0·2	150·43	Tm	168·91±0·05	169·4
Eu	151·90±0·03	152·0	Yt	173·2 ±0·2	173·04
Gd	156·9 ±0·2	157·3	Lu	174·91±0·05	175·0

The abundance ratio $O^{16} : O^{18}$ has been redetermined twice during the period under review. W. R. Smythe,[9] preparing the gas by decomposition of lead dioxide, reports 503 ± 10, D. I. Eropkin and V. N. Kondrateev,[10] from atmospheric absorption spectra, have obtained 595. The best value of the Naudé correction factor[11] remains, therefore, about 1·0002. W. R. Smythe has suggested reasons why his value for the isotopic ratio might be expected to differ from the normal, but these do not appear to be substantiated by the work of H. S. Taylor and A. J. Gould,[12] who consider the most trustworthy value at present to be 514 ± 13 (see further, this vol., p. 98).

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[4] A comprehensive survey of methods and results has also been given by J. Mattauch, *Physikal. Z.*, 1934, **35**, 567; *A.*, 937.

[5] *Z. anorg. Chem.*, 1933, **214**, 97; *A.*, 1933, 1099.

[6] *J.*, 1934, 499; *A.*, 713.

[7] G. P. Baxter and J. S. Thomas, *J. Amer. Chem. Soc.*, 1934, **56**, 1108; *A.*, 713.

[8] See this vol., p. 94, for discussion of certain other atomic weights.

[9] *Physical Rev.*, 1934, [ii], **45**, 299; *A.*, 469.

Abundance ratios for other light elements have also been redetermined. From intensity measurements on the lithium resonance line, L. S. Ornstein, J. A. Vreeswijk, jun., and G. Wolfsohn[13] obtain $Li^7 : Li^6 = 8{\cdot}1 \pm 0{\cdot}4$, in agreement with previous optical determinations,[14] but new mass-spectrograph experiments of A. K. Brewer and P. D. Kueck[15] lead to the ratio $12{\cdot}14 \pm 0{\cdot}4 : 1$, substantially confirming all earlier estimates by this more direct method.[16] The latter authors have also determined the ratios $K^{39} : K^{41}$ and $Rb^{85} : Rb^{87}$, obtaining $13{\cdot}9 \pm 0{\cdot}4$ and $2{\cdot}59 \pm 0{\cdot}04$, respectively. Earlier measurements of A. J. Dempster[17] and F. W. Aston[18] indicate 18 : 1 and 3·0 : 1 for these two elements.[19]

The results of W. W. Lozier, P. T. Smith, and W. Bleakney[3] for $H^1 : H^3$ are included in Table I. The same workers with G. P. Harnwell and H. D. Smyth[20] are also responsible for the negative data concerning He^3 and He^5, to which reference has already been made. They find $He^4 : He^3 > 10^5$, $He^4 : He^5 > 10^6$ for naturally occurring helium. Preliminary reports concerning carbon, nitrogen, neon, and argon are due to A. L. Vaughan, J. H. Williams, and J. T. Tate;[21] their values, obtained by mass analysis, are $C^{12} : C^{13} = 91{\cdot}6 \pm 2{\cdot}2$, $N^{14} : N^{15} = 265 \pm 8$, $Ne^{20} : Ne^{21} = 337 \pm 20$, $Ne^{20} : Ne^{22} = 9{\cdot}25 \pm 0{\cdot}08$, and $A^{40} : A^{36} = 304 \pm 12$. F. W. Aston[22] has obtained 140 ± 14 for $C^{12} : C^{13}$. The previously accepted ratio was 106 : 1.[23] For nitrogen the ratio 265 : 1 is, again, much lower than the last recognised value, about 330 : 1, itself only one-half the original estimates. The relative abundance of Ne^{22} appears to be a little greater, and that of Ne^{21} considerably smaller, than was previously believed. The argon determination, on the other hand, is the first of any reliability; it gives A^{36} a lower abundance than has sometimes been supposed.

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[10] *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **1**, 445; *A.*, 580.

[11] *Ann. Reports*, 1932, **29**, 305.

[12] *J. Amer. Chem. Soc.*, 1934, **56**, 1823; *A.*, 1082; see also R. Klar and A. Krauss, *Naturwiss.*, 1934, **22**, 119; *A.*, 377.

[13] *Physica*, 1933, **1**, 53; *A.*, 127.

[14] *Ann. Reports*, 1932, **29**, 304.

[15] *Physical Rev.*, 1934, [ii], **46**, 894.

[16] *Ann. Reports*, 1933, **30**, 348.

[17] *Physical Rev.*, 1922, [ii], **20**, 631; *A.*, 1923, ii, 413.

[18] *Proc. Roy. Soc.*, 1932, [*A*], **134**, 571; *A.*, 1932, 209.

[19] A curve given by W. R. Smythe, L. H. Rumbaugh, and S. S. West (*Physical Rev.*, 1934, [ii], **45**, 724; *A.*, 860) appears to favour the value of Brewer and Kueck against that of Dempster.

[20] *Physical Rev.*, 1934, [ii], **46**, 81.

[21] *Ibid.*, p. 327.

[22] *Nature*, 1934, **134**, 178; *A.*, 937.

The position regarding the magneto-optic method of analysis [24] has become somewhat clearer during the year. J. Papish and A. C. Shuman [25] have had the opportunity of testing the apparatus used in the Alabama Polytechnic Institute. Their report is entirely unfavourable. Similarly, comparison of F. W. Aston's work on calcium [26] with that of F. Allison and R. Goslin [27] is sufficient comment on the great sensitivity which these authors claim for their method. (Frau) I. Noddack [28] has also made a critical survey of the evidence in favour of the existence of new elements recently reported as discovered; the conclusion is against the present identification of elements of atomic number 61, 85, and 87.

Mechanical and Magnetic Moments of Nuclei.—In addition to the two scalar quantities, mass and electric charge, two vector quantities are required in order to describe in detail the interaction between the nucleus of an atom and its extranuclear electrons. These two quantities are the mechanical and the magnetic moment of the nucleus. As is the case with the scalar quantities, the magnitude of one of these vectors is restricted to integral multiples of the fundamental unit for all nuclei, whilst that of the other is not so restricted. The mechanical moment (total angular momentum) of any nucleus is integral in terms of $h/4\pi$, h being Planck's constant.

Hitherto, experiments in this field of nuclear research have not been reported upon in the present series of reports,[29] but the body of trustworthy data is now so large, and the methods of attack already of such variety, that some reference must be made to them and to the results. The latter have been collected from time to time in recent years,[30] but much new material has accumulated since the latest of these surveys.

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[23] *Ann. Reports*, 1933, **30**, 348.

[24] *Ibid.*, p. 349.

[25] *Science*, 1934, **79**, 297; *A.*, 625.

[26] *Nature*, 1934, **133**, 684; *A.*, 713.

[27] *Physical Rev.*, 1932, [ii], **40**, 1015; *A.*, 1933, 1223.

[28] *Angew. Chem.*, 1934, **47**, 301; *A.*, 853.

[29] See, however, *Ann. Reports*, 1932, **29**, 17; 1933, **30**, 76 *et seq.*

[30] H. Kallmann and H. Schüler, *Ergeb. exakt. Naturwiss.*, 1932, **11**, 134; G. Beck, Marx, " Handbuch der Radiologie," VI, (1), 1933, 279; N. F. Mott, " Handbuch der Physik," XXIV, (1), 1933, 785; F. W. Aston, " Mass Spectra and Isotopes," 1933, chaps. 15, 16; H. Schüler, *Z. Physik*, 1934, **88**, 323; *A.*, 580.

Until recently,[31] only two experimental methods were available. By measurement of the alternating intensities of the lines forming the rotational structure of the band spectrum of an elementary diatomic molecule, it is possible to calculate the value of the mechanical moment (I) of the nucleus concerned. However, the difference in intensity between neighbouring lines is small when the mechanical moment is at all considerable, and it is with only a few elements that diatomic molecules are formed which give rise to band spectra suitable for investigation. The second method involves the examination of the hyperfine structure of atomic spectral lines. Then, so long as the magnetic moment (μ) is not too small, I may be deduced unambiguously from the complexity of the hyperfine structure of certain lines, though a knowledge of the corresponding structure of other lines in the same spectrum may yield no definite information on this point. In favourable circumstances it is possible to calculate μ from measurements on the hyperfine structure separations.[32] The underlying theory, however, is intricate and an accuracy of a few units % is all that can be claimed in most cases. Quite recently, however, two other methods, of possibly more general applicability, have been successfully developed. They may be referred to as the methods of polarised resonance radiation and of atomic beams. The former method was applied to the sodium-D resonance radiation by N. P. Heydenburg, L. Larrick, and A. Ellett,[33] who measured the percentage polarisation for plane-polarised exciting radiation and zero magnetic field. It was hoped that measurements in these conditions would enable I to be evaluated, whilst similar observations with non-zero fields might lead to an estimate of μ. At first, the method yielded unacceptable results, but now, after more precise consideration of the underlying theory,[34] the discrepancies have been removed. The method appears to be chiefly useful for the evaluation of μ when I is known. The small differences in form of the ideal polarisation–magnetic field curves for different I values do not at present appear decisive enough for use in determining I, since many departures from ideal simplicity frequently characterise the experimental conditions.

The method of atomic beams has very direct affinities with the hyperfine structure method of investigation. Thus I may be determined, if μ is not too small, merely by counting the number of lines in a deflexion pattern, whilst, for the calculation of μ from observed separations, the same detailed information is required as is needed for the similar calculation from hyperfine-structure data. There is one difference, however : the axis of the magnetic moment of the nucleus may be in the same direction as that of the mechanical moment, or in the opposite direction (negative magnetic moment). This ambiguity of sign may be settled from observations on the hyperfine-structure pattern, but it remains unresolved when μ is obtained by the method of atomic beams. The suggestion that the arrangement of W. Gerlach and O. Stern might be modified for the purpose of determining I—and so μ—was put forward first by G. Breit and I. I. Rabi.[35] This is the method which has just been described. It differs in essentials from another molecular-beam method applied by O. Stern and his collaborators [36] to the determination of the magnetic moments of the nuclei H^1 and H^2. In this method, the nuclear moment is obtained when the effective magnetic moment of the molecule has been corrected for the rotational component. This correction was directly made in the case of hydrogen by making observations with ortho- and para-hydrogen in turn. The results, however, again are ambiguous with regard to sign.

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[31] See W. E. Curtis, *Nature*, 1934, **133**, 256; *A.*, 340.

[32] E. Fermi and E. Segrè, *Z. Physik*, 1933, **82**, 729; *A.*, 1933, 759; *Mem. R. Accad. d'Italia Sci. fis.*, 1933, **4**, 131; *A.*, 231.

[33] *Physical Rev.*, 1932, [ii], **40**, 1041; *A.*, 1933, 1220.

[34] See G. Breit, *Rev. Mod. Physics*, 1933, **5**, 91 (VII, §4).

The data of Table III refer chiefly to atomic species of odd mass number. Those of even mass number, with the exception of

TABLE III.*

	I.				
Nuclear species.	B.	H.	O.	μ.	References.
n^1	—	—	$\frac{1}{2}$	—	—
H^1	$\frac{1}{2}$	—	—	3·2, 2·5	36, 42
H^2	1	—	—	0·7	36, 42, 43
He^4	0	—	—	—	—
Li^7	$\frac{3}{2}$	$\frac{3}{2}$	—	3·3	44
Be^9	—	($\frac{1}{2}$)	—	—	45
C^{12}	0	—	—	—	—
N^{14}	1	—	—	$<0·2$	46
O^{16}	0	—	—	—	—
F^{19}	$\frac{1}{2}$	$\frac{1}{2}$	—	—	47
Na^{23}	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	2·5	48, 49, 50, 51
Mg	—	—	—	$\ll 1$	52
Al^{27}	—	$\frac{1}{2}$	—	1·9	—
P^{31}	$\frac{1}{2}$	—	—	—	53
S^{32}	0	—	—	—	—
Cl^{35}	$\frac{5}{2}$	—	—	—	—
K^{39}	$>\frac{1}{2}$	—	$\frac{3}{2}$	0·4	54, 55
Sc^{45}	—	$\frac{7}{2}$	—	3·6	56, 57

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[35] *Physical Rev.*, 1931, [ii], **38**, 2082.

[36] R. Frisch and O. Stern, *Z. Physik*, 1933, **85**, 4; I. Estermann and O. Stern, *ibid.*, p. 17; **86**, 132; *Nature*, 1934, **133**, 911; *A.*, 1933, 996, 1226; 1934, 828.

TABLE III.*—*Continued.*

Nuclear species.	*I.* B.	*I.* H.	*I.* O.	μ.	References.
V^{51}	—	$\frac{7}{2}$	—	—	58, 59
Mn^{55}	—	$\frac{5}{2}$	—	—	—
Co^{59}	—	$\frac{7}{2}$	—	2—3	60, 61
Cu^{63}	—	$\frac{3}{2}$	—	2·7	—
Cu^{65}	—	$\frac{3}{2}$	—	2·7	—
Zn^{67}	—	$\frac{5}{2}$	—	—	62
Ga^{69}	—	$\frac{3}{2}$	—	2·1	—
Ga^{71}	—	$\frac{3}{2}$	—	2·7	—
As^{75}	—	$\frac{3}{2}$	—	0·9	—
Br^{79}	—	$\frac{3}{2}$	—	—	—
Se^{80}	0	—	—	—	63
Br^{81}	—	$\frac{3}{2}$	—	—	—
Kr^{83}	—	$\frac{9}{2}$	—	—	64
Rb^{85}	—	$\frac{5}{2}$	—	—	65
Rb^{87}	—	$\frac{3}{2}$	—	—	65
Sr^{87}	—	$\geqslant\frac{3}{2}$	—	(−0·9)	
Nb^{93}	—	$\frac{9}{2}$	—	3·7	66
Mo^{95}	—	$\frac{1}{2}$	—	—	67
Mo^{97}	—	$\frac{1}{2}$	—	—	67
Ag^{107}	—	—	—	$<0{\cdot}3$	52
Ag^{109}	—	—	—	$<0{\cdot}3$	52
Cd^{111}	—	$\frac{1}{2}$	—	−0·6	—
Cd^{113}	—	$\frac{1}{2}$	—	−0·6	—
In^{115}	—	$\frac{9}{2}$	—	5·3	68
Sn^{117}	—	$\frac{1}{2}$	—	−0·9	69
Sn^{119}	—	$\frac{1}{2}$	—	−0·9	69
Sb^{121}	—	$\frac{5}{2}$	—	2·7	—
Sb^{123}	—	$\frac{7}{2}$	—	2·1	70
I^{127}	$\geqslant\frac{5}{2}$	$\frac{5}{2}$	—	—	71
Xe^{129}	—	$\frac{1}{2}$	—	$\left.\frac{\mu_{129}}{\mu_{131}}\right\} = 1{\cdot}1$	72, 73
Xe^{131}	—	$\frac{3}{2}$	—		72, 73
Cs^{133}	—	$\frac{7}{2}$	$\frac{7}{2}$	2·7	74—78
Ba^{137}	—	$\frac{3}{2}$	—	0·9	—
La^{139}	—	$\frac{7}{2}$	—	2·5	79, 80
Pr^{141}	—	$\frac{5}{2}$	—	—	—
Tb^{159}	—	$\frac{3}{2}$	—	—	81
Tm^{169}	—	$\frac{1}{2}$	—	—	82
Lu^{175}	—	$\frac{5}{2}$	—	—	83
Ta^{181}	—	$\frac{7}{2}$	—	—	84
W^{183}	—	$\frac{1}{2}$	—	—	67
Re^{185}	—	$\frac{5}{2}$	—	—	—
Re^{187}	—	$\frac{5}{2}$	—	—	—
Au^{197}	—	$\frac{3}{2}$	—	0·2	—
Hg^{199}	—	$\frac{1}{2}$	—	0·6	—
Hg^{201}	—	$\frac{3}{2}$	—	−0·6	—
Tl^{203}	—	$\frac{1}{2}$	—	1·4	85
Tl^{205}	—	$\frac{1}{2}$	—	1·4	85
Pb^{207}	—	$\frac{1}{2}$	—	0·6	—
Bi^{209}	—	$\frac{9}{2}$	—	3·6	—
Pa^{231}	—	$\frac{3}{2}$	—	—	86

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* The values of I are given in units of $h/2\pi$, those of μ in protonic magnetons, *i.e.*, in terms of $eh/4\pi Mc$. B, H, and O refer, respectively, to determinations from band spectra, hyperfine structure, and other methods. References are given where they are not included in one of the surveys already quoted.

H^2, Li^6, B^{10}, and N^{14}, have even atomic number also, and it has generally been assumed that such nuclei (having both atomic and mass numbers even) are without mechanical moment. The data available concerning the lighter nuclei confirm this hypothesis, yet it must be admitted that, for the heavier species, it remains pure assumption. The experimental facts are that it has always been possible, hitherto, to interpret hyperfine-structure patterns in complex atomic spectra on the assumption that the true hyperfine structure (as distinct from any structure due to isotope displacement) was to be ascribed entirely to the emission from atoms for which the mass number was odd. Whatever may be the final conclusion, at present no data exist which run contrary to this assumption.[37]

Of the data contained in Table III, the most unexpected, and at the same time the most important for developing a theory of the nucleus, are the values of the nuclear magnetic moments for the two more abundant isotopes of hydrogen. The magnetic moment of the proton is not, as was anticipated, one protonic magneton. Concerning the relative values for the hydrogen isotopes, there is strong confirmatory evidence from the experiments of A. Farkas, L. Farkas, and P. Harteck [38] on the rate of reconversion of orthohydrogen into normal hydrogen by (paramagnetic) molecular oxygen. This rate is 16 times greater for H^1_2 than it is for H^2_2. From this result, F. Kalckar and E. Teller [39] conclude that the ratio of the nuclear magnetic moments is 4 : 1, in good agreement with the direct determinations.

As has been indicated, the analysis and interpretation of hyperfine structure patterns are in terms of " magnetic splitting " of the atomic energy levels, for a single type of atom, complicated, in cases where two or more isotopes are present, by " isotope displacement " of corresponding energy levels as between atoms of the different isotopic species. Regularities in this displacement structure where several isotopes are present have been noted, a general basis of interpretation having been advanced by G. Breit.[40] The relative stabilities (mass-defects) of two nuclear species appear to be important in determining the isotope displacement. Thus, in general, the difference in respect of stability between species of odd and even mass number shows up in the displacement pattern.

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[37] G. Gamow (*Proc. Roy. Soc.*, 1934, [*A*], **146**, 217; *A.*, 1152) suggests, in an interpretation of the data concerning radioactive β-disintegrations, that Pb^{208} has a nuclear spin of 1 unit. M. Goldhaber (*Proc. Camb. Phil. Soc.*, 1934, **30**, 561) has assigned a similar value to Li^6 from a consideration of the relative probabilities of certain cases of artificial disintegration.

[38] *Proc. Roy. Soc.*, 1934, [*A*], **144**, 481; *A.*, 608.

[39] *Nature*, 1934, **134**, 180; *A.*, 940. [40] *Physical Rev.*, 1934, [ii], **46**, 319.

Here the recent observations of H. Schüler and T. Schmidt[41] on samarium are of considerable interest. These authors find a large anomaly in the displacements amongst the isotopes of even mass number. It seems that a change of nuclear structure sets in between Sm^{150} and Sm^{152}, most likely with a decrease in stability at some intermediate stage. They suggest, therefore, that the α-particle activity of samarium is to be ascribed to Sm^{151}, present in very small amount, or to Sm^{152}. They make the suggestion that the α-activity of samarium, the β-activity of neodymium, and the extreme scarceness of element 61 upon the earth might not be disconnected facts. A single transformation chain, $Sm^{151} \xrightarrow{\alpha} Nd^{147} \xrightarrow{\beta} Il^{147} \xrightarrow{\beta} Sm^{147}$, for example, would suffice to correlate these observations.

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[41] *Z. Physik*, 1934, **92**, 148.

[42] I. I. Rabi, J. M. B. Kellogg, and J. R. Zacharias, *Physical Rev.*, 1934, [ii], **46**, 157, 163; *A.*, 1153.

[43] G. M. Murphy and (Miss) H. Johnston, *ibid.*, p. 95; *A.*, 1051.

[44] N. M. Gray, *ibid.*, 1933, [ii], **44**, 570; *A.*, 1933, 1219.

[45] A. E. Parker, *ibid.*, **43**, 1035.

[46] R. F. Bacher, *ibid.*, p. 1001; *A.*, 1933, 767.

[47] J. S. Campbell, *Z. Physik*, 1933, **84**, 393; *A.*, 1933, 991.

[48] J. Joffe, *Physical Rev.*, 1934, [ii], **45**, 468; *A.*, 575.

[49] L. P. Granath and C. M. van Atta, *ibid.*, 1933, [ii], **44**, 935; *A.*, 124.

[50] L. Larrick, *ibid.*, 1934, [ii], **46**, 581; A. Ellett and N. P. Heydenburg, *ibid.*, p. 583.

[51] I. I. Rabi and V. W. Cohen, *ibid.*, p. 707.

[52] S. Frisch and V. A. Matveev, *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **1**, 460; *A.*, 576.

[53] (Miss) M. F. Ashley, *Physical Rev.*, 1933, [ii], **44**, 919; *A.*, 124.

[54] S. Millman, M. Fox, and I. I. Rabi, *ibid.*, 1934, [ii], **46**, 320.

[55] D. A. Jackson and H. Kuhn, *Nature*, 1934, **134**, 25.

[56] H. Kopfermann and E. Rasmusson, *Z. Physik*, 1934, **92**, 82.

[57] H. Schüler and T. Schmidt, *Naturwiss.*, 1934, **22**, 758.

[58] H. E. White, *Physical Rev.*, 1932, [ii], **40**, 1041; *A.*, 1933, 1221.

[59] H. Kopfermann and E. Rasmussen, *Naturwiss.*, 1934, **22**, 418.

[60] K. R. More, *Physical Rev.*, 1934, [ii], **46**, 470.

[61] H. Kopfermann and E. Rasmussen, *Naturwiss.*, 1934, **22**, 291.

[62] H. Schüler and H. Westmeyer, *Z. Physik*, 1933, **81**, 565; *A.*, 1933, 547.

[63] E. Olsson, *ibid.*, 1934, **90**, 138; *A.*, 1051.

[64] H. Kopfermann and N. Wieth-Knudsen, *ibid.*, 1933, **85**, 353; *A.*, 1933, 1095.

[65] D. A. Jackson, *ibid.*, **86**, 131; *A.*, 1933, 1221.

[66] S. S. Ballard, *Physical Rev.*, 1934, [ii], **46**, 806.

[67] N. S. Grace and K. R. More, *ibid.*, **45**, 166; *A.*, 339.

[68] F. Paschen and J. S. Campbell, *Naturwiss.*, 1934, **22**, 136; *A.*, 467.

[69] S. Tolansky, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 574; *A.*, 823.

[70] *Idem*, *ibid.*, **146**, 182; *A.*, 1147.

[71] *Idem*, *Nature*, 1934, **134**, 851.

[72] E. G. Jones, *ibid.*, 1933, **132**, 781; *A.*, 1934, 2; *Proc. Roy. Soc.*, 1934, [*A*], **144**, 587; *A.*, 823.

[73] H. Kopfermann and E. Rindal, *Z. Physik*, 1934, **87**, 460; *A.*, 339.

[74] D. A. Jackson, *Proc. Roy. Soc.*, 1934, [*A*], **143**, 455; *A.*, 232.

[75] V. W. Cohen, *Physical Rev.*, 1934, [ii], **46**, 713.

[76] N. P. Heydenburg, *ibid.*, p. 802.

[77] L. P. Granath and R. K. Stranathan, *ibid.*, p. 317.

[78] D. A. Jackson, *Proc. Roy. Soc.*, 1934, [*A*], **147**, 500.

[79] O. E. Anderson, *Physical Rev.*, 1934, [ii], **45**, 685; *A.*, 824.

[80] *Idem*, *ibid.*, **46**, 473.

[81] H. Schüler and H. Gollnow, *Naturwiss.*, 1934, **22**, 730.

[82] H. Schüler and T. Schmidt, *ibid.*, p. 838.

[83] *Idem*, *ibid.*, p. 714.

[84] J. H. Gisolf and P. Zeeman, *Nature*, 1933, **132**, 566; *A.*, 1933, 1219.

[85] L. A. Wills, *Physical Rev.*, 1934, [ii], **45**, 883; *A.*, 940.

[86] H. Schüler and H. Gollnow, *Naturwiss.*, 1934, **22**, 511; *A.*, 937.

The Separation of Isotopes.—In addition to the many physico-chemical and chemical methods developed primarily for the concentration of the heavier isotopes of hydrogen [87] (nearly 50 papers on this subject are represented in the Abstracts for 1933), two successful attempts have been made at separation by purely physical means.[19, 88] In effect, these methods employ mass analysis by some combination of electric and magnetic fields, the design of the apparatus being such that very intense ion beams may be passed. Up to the present, however, separation has been effected only with lithium and potassium. G. Hertz [89] has applied his diffusion method [90] to the production of spectroscopically pure H^2 and, recently, with an enlarged apparatus,[91] has obtained Ne^{22} very nearly free from the other isotopes of neon.

Natural Radioactivity of the Lighter Elements.

Potassium and Rubidium.—The occurrence of these medium-heavy, β-active nuclei of long life has hitherto presented an unsolved problem. Now, in the light of a fairly successful theory of β-disintegration (see below) and rapidly increasing knowledge of artificially produced radioactive species of rapid decay, this problem can be considered in its true perspective. G. Gamow [92] has indicated three possible solutions. There may be simultaneous emission of two β-particles (*e.g.*, $K^{41} \longrightarrow Sc^{41} + 2e$), or the long period may be that of a preceding α-particle change (*e.g.*, $K^{40} \longrightarrow Cl^{36} + He^4 \longrightarrow A^{36} + He^4 + e$), or the mechanical moments of initial and final nuclei (*e.g.*, K^{41} and Ca^{41}) may differ considerably.

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[87] See *Ann. Reports*, 1932, **29**, 302.

[88] M. L. E. Oliphant, E. S. Shire, and B. M. Crowther, *Nature*, 1934, **133**, 377; *A.*, 343; *Proc. Roy. Soc.*, 1934, [*A*], **146**, 922.

[89] *Naturwiss.*, 1933, **21**, 884; *A.*, 156.

[90] *Ann. Reports*, 1932, **29**, 303.

[91] H. Harmsen, G. Hertz, and W. Schütze, *Z. Physik*, 1934, **90**, 703; *A.*, 1185.

[92] *Nature*, 1934, **133**, 744; *A.*, 714.

G. von Hevesy, M. Pahl, and R. Hosemann [93] have tested certain of these possibilities. They find evidence of two groups of electrons (though not in equal numbers)—as did D. Bocciarelli [94]—but there are no α-particles. No short-lived bromine isotope is formed from rubidium, nor short-lived calcium isotope from potassium. Isotopic fractionation of potassium merely proves that K^{39} is inactive. F. W. Aston [95] finds no appreciable Ca^{41} in old potassium-rich biotites. The problem has been defined but not solved.

Samarium.—The report of M. Mäder [96] of the emission of radiation of two types, α-particles of range 1·16 cm. of standard air and protons of range 1·37 cm., has not been confirmed. G. Ortner and J. Schintlmeister [97] failed to find any indication of the second type of radiation. They estimate a range of 1·16 cm. of air at *S.T.P.* for the α-particles. A somewhat higher value has been obtained by H. Herszfinkiel and A. Wroncberg [98] (1·67 cm.), but W. F. Libby [99] is in favour of the lower value (1·23 cm.). The activity determined by G. von Hevesy and M. Pahl [1] (75 α-particles per g. per sec.) is approximately confirmed by the work of H. Herszfinkiel and A. Wroncberg,[98] although an activity almost twice as great is reported by W. F. Libby.[99] The total activity as measured by M. Mäder [96] is of the same high order.

Neodymium and Other Rare-earth Elements.—By repeated fractionation of a rare-earth mixture, L. Rolla and L. Mazza [2] conclude that the feeble activity often associated with neodymium is probably not specific. G. von Hevesy and M. Pahl [3] draw similar conclusions from very similar experiments: the activity of samarium is much greater than that of any other rare-earth element. W. F. Libby,[99] however, believes that a thick-layer activity about one-tenth of that of samarium (estimated as number of disintegrations per sec.) is specific to neodymium. He considers that this is a β-particle activity, magnetic-deflection and absorption measurements both suggesting an energy of about 10^4 electron-volts for the electrons. A half-value period of about 10^{12} years is suggested. The thick-layer activities of praseodymium and gadolinium are at least twenty times smaller.

Beryllium.—Following the report of R. M. Langer and R. W.

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[93] *Nature*, 1934, **134**, 377; *A.*, 1150.

[94] *Atti R. Accad. Lincei*, 1933, [vi], **17**, 830; *A.*, 1933, 995.

[95] *Nature*, 1934, **133**, 869; *A.*, 825.

[96] *Z. Physik*, 1934, **88**, 601; *A.*, 713.

[97] *Ibid.*, **90**, 698; *A.*, 1150.

[98] *Compt. rend.*, 1934, **199**, 133; *A.*, 1053.

[99] *Physical Rev.*, 1934, [ii], **46**, 196; *A.*, 1150.

[1] *Ann. Reports*, 1933, **30**, 344.

[2] *Atti R. Accad. Lincei*, 1933, [vi], **18**, 472; *A.*, 578.

[3] *Z. physikal. Chem.*, 1934, **169**, 147; *A.*, 937.

Raitt[4] of an α-activity from beryllium (half-value period $\sim 10^{14}$ years), various workers have attempted to confirm these observations but failed to do so.[99, 5] If α-particles of range greater than 1 cm. are emitted, then the half-value period must be greater than 10^{15} years; if the particles have a range of 1 mm., then the minimum allowable period is 10^{14} years. However, on any reasonable assumption, unless α-particles are emitted with much less than 2×10^4 e.v. energy (0·4 mm. range), the period should be of the order of seconds rather than millenniums. The extensive observations of (Lord) Rayleigh on the helium content of beryl,[6] indicating a definite correlation between amount of helium and mineral age, appear therefore as more conclusive evidence for the α-activity of beryllium than the other experiments are to the contrary. Ascribing the activity to Be^9, and calculating from the maximum helium content observed, a half-value period of the order of 10^{12} years is obtained, though to assume Be^8 and $\tau \sim 10^9$ years would do equally well. It seems unlikely that the discovery of the photo-disintegration of Be^9 (see below) will seriously affect the interpretation of these results.

Zinc.—H. Fesefeldt[7] has shown that any α-emission from zinc cannot be greater than one-tenth of that reported by H. Ziegert.[8]

α-Activities of Unknown Origin.—G. Dieck[9] and A. V. Grosse[10] have reported such α-activities, the former from surfaces of copper and gold, and the latter from the mineral eudyalite, associated with the actinium-containing samples in chemical analysis.

Radioactivity of the Heavy Elements: New Data.

No details concerning this branch of the subject were given in the last report. Now, after a period of relative inactivity, it is probable that the experimental attack will be renewed in certain directions owing to the interest aroused by the new theories of β-decay and the possibility of assigning quantum specifications to the nuclear-excited states which result in γ-ray emission. The theories of β-disintegration will be described in another place; here we are concerned chiefly with the new experimental data which have been collected in the two years which have passed since the last report.[11]

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[4] *Physical Rev.*, 1933, [ii], **43**, 585.

[5] (Lord) Rayleigh, *Nature*, 1933, **131**, 724; *A.*, 1933, 692; R. D. Evans and M. C. Henderson, *Physical Rev.*, 1933, [ii], **44**, 59; D. M. Gans, W. D. Harkins, and H. W. Newson, *ibid.*, p. 310.

[6] *Proc. Roy. Soc.*, 1933, [*A*], **142**, 370; *A.*, 1934, 53.

[7] *Z. Physik*, 1933, **86**, 611; *A.*, 127.

[8] *Ibid.*, 1928, **46**, 668; *A.*, 1928, 455.

[9] *Naturwiss.*, 1933, **21**, 896; *A.*, 127.

[10] *J. Amer. Chem. Soc.*, 1934, **56**, 1922; *A.*, 1150.

Redeterminations of half-value periods have been made as follows: for uranium-*I*, F. Western and A. E. Ruark [12] obtain $(4{\cdot}58 \pm 0{\cdot}09) \times 10^9$ years, in good agreement with the value found by A. F. Kovarik and N. I. Adams; [13] O. A. Gratias [14] reports $1{\cdot}70 \times 10^5$ years for uranium-*II*, pointing out the source of error in C. H. Collie's [15] recent determination; J. C. Jacobsen,[16] having met the criticism directed against his earlier methods, gives 2×10^{-4} sec. as the most probable value for radium-C'; $22{\cdot}3 \pm 0{\cdot}04$ years is reported by E. Walling [17] for radium-*D*; the value for actinouranium, according to F. Western and A. E. Ruark,[18] is roughly 4×10^8 years, and to thorium a half-value period of $1{\cdot}3 \times 10^{10}$ years is assigned.[19]

Considerable progress has been made in the period under review with the magnetic-velocity analysis of the α-particle emission from a large number of substances. The first application to this problem of the semicircular focusing method dates from 1929. S. Rosenblum [20] employed the large general-purposes electromagnet of the Paris Academy of Sciences, with photographic registration. A special-purpose electromagnet, designed by J. D. Cockcroft [21] for use with electrical counting systems, was installed in the Cavendish Laboratory in 1932. It has been employed by (Lord) Rutherford, C. E. Wynn-Williams, W. B. Lewis, and B. V. Bowden,[22] Rutherford, Lewis, and Bowden,[23] and Lewis and Bowden [24] for investigations of the "normal" and "long-range" α-particle emission of the chief members of the radium and thorium series. In the last of their publications [24] are collected the complete results to date, together with the data of S. Rosenblum (concerning members of the actinium series also), and the best values of mean ranges in standard air as previously determined.[25] High-accuracy determinations of the relative velocities of the α-particles from radon, radium-*A*, and radium-*C′* have also been made, using the direct deviation method, by G. H. Briggs,[26] in continuation of earlier work. Some evidence for the emission of long-range α-particles by actinium-*C′* (roughly 9 in 10^5 normal α-particles from actinium-*C′*) has been obtained by (Mme.) P. Curie and (Mlle.) W. A. Lub.[27] R. Naidu[28] has established the ionisation–distance (Bragg) curves for polonium α-particles in the five rare gases, and G. Mano[29] the velocity–distance curves for the α-particles of thorium-*C′* traversing air, hydrogen, helium, neon, and argon. New and quantitative investigations on pleochroic haloes (due to the action of α-particles, from radioactive inclusions, on mica) have been reported by G. H. Henderson with S. Bateson[30] and with L. G. Turnbull.[31]

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[11] *Ann. Reports*, 1932, **29**, 308.
[12] *Physical Rev.*, 1933, [ii], **44**, 675; *A.*, 1933, 1224.
[13] *Ibid.*, 1932, [ii], **40**, 718; *A.*, 1932, 790.
[14] *Phil. Mag.*, 1934, [vii], **17**, 491; *A.*, 343.
[15] *Proc. Roy. Soc.*, 1931, [*A*], **131**, 541; *A.*, 1931, 891.
[16] *Nature*, 1934, **133**, 565; *A.*, 578.
[17] *Z. Physik*, 1934, **87**, 603; *A.*, 343.
[18] *Physical Rev.*, 1934, [ii], **45**, 628; *A.*, 713.
[19] H. Fesefeldt, *Z. Physik*, 1933, **86**, 605; *A.*, 127.
[20] *Compt. rend.*, 1929, **188**, 1401; *A.*, 1929, 738.
[21] *J. Sci. Instr.*, 1933, **10**, 71; *A.*, 1933, 367.
[22] *Proc. Roy. Soc.*, 1933, [*A*], **139**, 617; *A.*, 1933, 443.
[23] *Ibid.*, **142**, 347; *A.*, 1933, 1224.
[24] *Ibid.*, 1934, [*A*], **145**, 235; *A.*, 938.
[25] *Ann. Reports*, 1932, **29**, 309.

Fresh information concerning primary β-particle emission deals chiefly with the upper limits of energy in the continuous spectra. B. W. Sargent[32] carried out the determination of the upper limit for the β-particles of uranium-X_2 and reviewed all the data available at the time. He put forward very strong evidence for the reality of a close connexion, analogous to the Geiger–Nuttall relation, between disintegration constant and maximum β-particle energy. On plotting logarithms of these two quantities, it appeared that eleven points out of twelve (one for each β-active body considered) lay on one or other of two smooth curves. This demonstration proved to be one of the starting points of the recent theories of the β-particle disintegration.

Isolated investigations into the γ-radiation from certain elements have been made by all the standard methods, crystal diffraction,[33] absorption,[34] and measurement of the heating effect,[35] in addition to those made by the method of the natural β-ray spectrum. Interest chiefly centres in the latter measurements, however. C. D. Ellis[36] has reinvestigated completely the natural β-ray spectra of the *B* and *C* products in the radium and thorium series, whilst R. Arnoult[37] and K. C. Wang[38] have made measurements with thorium-active deposit. All these measurements are important for the interpretation of the complexity (fine structure) of normal α-particle groups and of the emission of long-range α-particles in certain cases.[39] Accurate numerical comparison[24] completely confirms the interpretations originally offered. Fine structure in the normal groups is present when the product nucleus is left excited after the emission of the α-particle; the presence of long-range groups, on the other hand, is evidence of states of excitation consequent upon the transformation preceding the α-particle change. In the two cases studied (radium-*C′* and thorium-*C′*), this transformation is of the β-particle type. The complexity of the normal groups is always of the nature of "fine structure" because the γ-rays associated with α-particle disintegrations are never of very high energy; yet the α-particles of the long-range groups would be even more infrequent than they are if there were not high-energy γ-rays associated with β-particle transformations. There is at present no explanation for this qualitative difference between radioactive changes of the two types, for the simplest assumption in either case is that the excitation of the nucleus is an excitation of α-particle levels. Evidence for previous or subsequent excitation of the nucleus shows up most clearly in α-particle disintegrations on account of the discrete energy groups of the emitted particles; there can be no doubt, however, that it is present, at least as regards subsequent excitation, in β-particle disintegrations, also.[40] Here, however, the complexity of the upper limits of the partial continuous spectra cannot be described as fine structure, for the reason already advanced.

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[26] *Proc. Roy. Soc.*, 1934, [*A*], **143**, 604; *A.*, 342.

[27] *J. Phys. Radium*, 1933, [vii], **4**, 513; *A.*, 1933, 1223.

[28] *Ibid.*, 1934, [vii], **5**, 343; *A.*, 1053; *Ann. Physique*, 1934, [xi], **1**, 72; *A.*, 235.

[29] *Ibid.*, p. 407; *A.*, 579.

[30] *Proc. Roy. Soc.*, 1934, [*A*], **145**, 563; *A.*, 1087.

[31] *Ibid.*, p. 582; *A.*, 1087.

[32] *Ibid.*, 1933, [*A*], **139**, 659; *A.*, 1933, 443.

[33] M. J. N. Valadares, *Ann. Physique*, 1934, [xi], **2**, 197; *A.*, 1151.

[34] (Mme.) P. Curie and P. Savel, *J. Phys. Radium*, 1933, [vii], **4**, 457; *A.*, 1933, 1224; E. Stahel and W. Johner, *ibid.*, 1934, [vii], **5**, 97; *A.*, 579.

[35] I. Zlotowski, *Compt. rend.*, 1934, **199**, 284; *A.*, 938.

[36] *Proc. Roy. Soc.*, 1932, [*A*], **138**, 318; *A.*, 1933, 4; *ibid.*, 1934, [*A*], **143**, 350; *A.*, 235.

Interpretation of the natural β-ray spectra, in so far as the determination of γ-ray energies is concerned, is relatively simple. In order to deduce intensities (quanta per disintegration), a theory of internal conversion is necessary. Internal conversion coefficients for the more intense components may be deduced experimentally from measurements on "excited" and natural β-ray spectra, respectively; for the rest, some satisfactory basis of interpolation is required. The early experiments showed[41] that no entirely trustworthy basis was provided by the experimental data alone.

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[37] *J. Phys. Radium*, 1934, [vii], **5**, 67; *A.*, 470; *Compt. rend.*, 1934, **198**, 1603; *A.*, 713.

[38] *Z. Physik*, 1934, **87**, 633; *A.*, 342.

[39] *Ann. Reports*, 1932, **29**, 310 *et seq.*

[40] C. D. Ellis and N. F. Mott, *Proc. Roy. Soc.*, 1933, [*A*], **141**, 502; *A.*, 1933, 1100.

[41] C. D. Ellis and G. H. Aston, *ibid.*, 1930, [*A*], **129**, 180; *A.*, 1930, 1339.

The relevant theory has been developed by H. R. Hulme,[42] H. M. Taylor and N. F. Mott,[43] J. B. Fisk,[44] and J. B. Fisk and H. M. Taylor.[45] Their value for the internal conversion coefficient depends very markedly upon the type of nuclear transition in which the γ-ray quantum is produced. For (electric) quadripole transitions, in which the nuclear azimuthal quantum number changes by 0 or 2, it is about three times greater than for dipole transitions, in which the change of spin is one unit.[46] Thus, spin changes may be assigned to the various transitions, some as the direct result of experimental determinations of internal conversion coefficients, others by a process of comparison of theoretical alternatives. When this has been done, two results emerge : internal conversion coefficients having been assigned to each component of the γ-radiation, absolute intensities may be deduced, and, secondly, relative spin values may be assigned to all the energy levels in the level system by which the transitions are described.[47] The data concerning long-range α-particles and natural β-ray groups are thus susceptible of comparison otherwise than as regards agreement of energy differences alone; from each set of data, excitation probabilities may be deduced for the different levels of the system. To do this requires, in the former case, a knowledge of the absolute values of the azimuthal quantum numbers concerned, and, in the latter, merely a knowledge of relative values. This detailed comparison of the two sets of data for radium-C' has been made by Rutherford, Lewis, and Bowden.[23] Other information concerning the spins of radioactive nuclei will be discussed in connexion with the theory of β-disintegration (see below).

Progress in the separation and purification of large quantities of protoactinium [48] has not reached the stage when an accurate value for the atomic weight may be obtained by chemical methods,[49] but the determination of nuclear spin by hyperfine-structure analysis [86] confirms the general expectation that the mass number is odd.

Nuclear Transformations produced by Fast Particles.

I. *The Production of Stable Species.*—In this section and in the next the effects produced by using α-particles, neutrons, protons, and deuterons [50] as projectiles will be considered in turn, only the work of the past year being described. Table III of the report for 1933 [51] summarises the principal transformations then known to occur; reference may be made to it for the earlier results.

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[42] *Proc. Roy. Soc.*, 1932, [*A*], **138**, 643; *A.*, 1933, 110.

[43] *Ibid.*, p. 665; *A.*, 1933, 111; 1933, [*A*], **142**, 215; *A.*, 1933, 1224.

[44] *Ibid.*, 1934, [*A*], **143**, 674; *A.*, 342.

[45] *Ibid.*, **146**, 178; *A.*, 1151.

[46] This result is complicated somewhat if the radiation fields describing the transitions involve magnetic multipole components, also.[45]

[47] C. D. Ellis and N. F. Mott, *Proc. Roy. Soc.*, 1933, [*A*], **139**, 369; *A.*, 1933, 204.

[48] G. Graue and H. Käding, *Naturwiss.*, 1934, **22**, 386; *A.*, 854.

[49] See *Ann. Reports*, 1933, **30**, 347.

α-Particles. New data have been obtained concerning the transformations produced by α-particles bombarding heavy hydrogen,[52] lithium,[53] beryllium,[54] boron,[55] nitrogen,[56] fluorine,[57] sodium,[58] magnesium,[59] aluminium,[60] and phosphorus.[61] Certain of these have been discussed, from a single viewpoint, by H. Pose.[62] The majority of the transformations studied have, as previously, been those in which the α-particle is captured, another particle, proton or neutron being emitted in the process. There is some evidence, however, that in certain cases (lithium, nitrogen, fluorine, and aluminium) the nucleus is excited without its capturing the α-particle, and in one case (heavy hydrogen) the results indicate disintegration, also without capture ($H^2 \longrightarrow H^1 + n^1$). For the rest, the information obtained may best be presented by tabulation. In Table IV are given particulars concerning potential barriers, as well as the maximum numbers of proton (or neutron) groups observed when α-particles of a single energy are employed. Nuclear symbols are listed in col. 1, and in cols. 2 and 3 are given, for each nucleus, the energies, in millions of electron-volts, which an α-particle must possess in order to enter, with reasonable probability, through the top of the barrier (2) and through the various resonance levels (3), respectively. Col. 4 indicates the number of groups (p = proton, n = neutron) in the energy spectrum of the particles emitted. The importance of an accurate knowledge of the numbers and positions of resonance levels lies in its direct relevance to any theory of nuclear structure which may be advanced.

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[50] This designation is here preferred to " diplon " and " deuton," frequently employed.

[51] *Ann. Reports*, 1933, **30**, 355.

[52] (Lord) Rutherford and A. E. Kempton, *Proc. Roy. Soc.*, 1934, [*A*], **143**, 724; *A.*, 342; J. R. Dunning, *Physical Rev.*, 1934, [ii], **45**, 586; *A.*, 714.

[53] P. Savel, *Compt. rend.*, 1934, **198**, 1404; *A.*, 579.

[54] J. Chadwick, *Proc. Roy. Soc.*, 1933, [*A*], **142**, 1; *A.*, 1933, 1224; G. Bernardini, *Z. Physik*, 1933, **85**, 555; *A.*, 1933, 1225; P. Auger, *J. Phys. Radium*, 1933, [vii], **4**, 718; *Compt. rend.*, 1934, **199**, 414; *A.*, 235, 1053; (Mlle.) M. Blau, *J. Phys. Radium*, 1934, [vii], **5**, 61; *A.*, 470; J. R. Dunning, *loc. cit.*; T. W. Bonner and L. M. Mott-Smith, *Physical Rev.*, 1934, [ii], **46**, 258; *A.*, 1151; H. R. Crane, C. C. Lauritsen, and A. Soltan, *ibid.*, **45**, 507; *A.*, 714.

[55] J. Chadwick, *loc. cit.*, F. Heidenreich, *Z. Physik*, 1933, **86**, 675; *A.*, 128; R. F. Paton, *Z. Physik*, 1934, **90**, 586; *A.*, 1151; H. Miller, W. E. Duncanson, and A. N. May, *Proc. Camb. Phil. Soc.*, 1934, **30**, 549.

[56] E. C. Pollard, *Proc. Roy. Soc.*, 1933, [*A*], **141**, 375; P. Savel, *loc. cit.*; H. Stegmann, *Physikal. Z.*, 1934, **35**, 636; *A.*, 1053.

[57] T. W. Bonner and L. M. Mott-Smith, *loc. cit.*

[58] A. König, *Naturwiss.*, 1934, **22**, 150; *Z. Physik*, 1934, **90**, 197; *A.*, 471, 1151; P. Savel, *loc. cit.*

[59] H. Klarmann, *Z. Physik*, 1934, **87**, 411; *A.*, 342; P. Savel, *loc. cit.*; W. E. Duncanson and H. Miller, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 396.

[60] P. Savel, *Compt. rend.*, 1934, **198**, 368; *A.*, 234; (Mlle.) M. Blau, *loc. cit.*; O. Haxel, *Z. Physik*, 1934, **88**, 346; **90**, 373; *A.*, 580, 1151; G. Ortner and G. Stetter, *ibid.*, 1934, **89**, 708; *A.*, 1053; W. E. Duncanson and H. Miller, *loc. cit.*

[61] R. F. Paton, *loc. cit.*

[62] *Physikal. Z.*, 1934, **35**, 633; *A.*, 1053.

Table IV.

Li^7	3·0	—	$1(n)$	F^{19}	5·0	4·0, 3·4	$\nless 2(p)$?(n)
Be^9	3·5	2·5, 1·4	$\nless 2(n)$	Na^{23}	—	$\nless 1$	$2(p)$?(n)
B^{10}	3·6	3·0	$5(p)$?(n)	Mg(?)	6·5	6·3, 5·7	$\nless 2(p)$?(n)
B^{11}	3·7	2·4	$1(n)$	Al^{27}	6·8	6·61, 5·75, 5·25, 4·86, 4·49, 4·0	$4(p)$?(n)
N^{14}	4·1	3·5	$1(p)$				
				P^{31}	—	—	$3(p)$?(n)

Neutrons. Information concerning the production of stable atomic species in neutron-produced transformations has hitherto been obtained entirely by means of the expansion chamber. By this method very little has recently been added to the data previously reported upon.[63] The use of more intense sources (*e.g.*, those obtained by bombarding beryllium with high-velocity deuterons) [64] and the knowledge that extremely slow neutrons are frequently much more effective than neutrons of high energy [65] will no doubt result in a renewal of activity in this field. One of the results which may then be anticipated is that additional information will accrue concerning the positions of resonance levels in the potential barriers of various light nuclei as against α-particles; for most of the neutron-produced disintegrations occur with emission of α-particles and, when one of these escapes as a disintegration particle with energy less than that which corresponds to the top of the barrier, it is probable that it leaves the product nucleus through one of the resonance levels. A statistic exhibiting the energies of the disintegration particles will thus allow the positions of the resonance levels to be deduced.

Evidence for a new mode of disintegration of carbon by neutrons has been obtained by J. Chadwick, N. Feather, and W. T. Davies.[66] Three tracks having a common origin are, most probably, to be interpreted in terms of the non-capture process $C^{12} \longrightarrow 3He^4$. It is possible that a similar interpretation holds for the triple fork photographed in an expansion chamber by L. Misovski, I. Kurtschatov, N. Dobrotin, and I. Gurevitsch.[67]

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[63] *Ann. Reports*, 1933, **30**, 352.

[64] F. N. D. Kurie, *Physical Rev.*, 1934, [ii], **45**, 904; *Bull. Amer. Physical Soc.*, 1934, **9**, (3), 8.

[65] E. Fermi, E. Amaldi, B. Pontecorvo, F. Rasetti, and E. Segrè, *La Ricerca Scient.*, 1934, **5**, (2), 282, 380.

[66] *Proc. Camb. Phil. Soc.*, 1934, **30**, 357.

Protons and deuterons. During the past year, a more extended study has been made of the disintegration effects observed with several of the lighter elements, and many new modes of transformation have been established. The transformations of heavy hydrogen,[68] lithium,[69] beryllium,[70] boron,[71] carbon,[72] and fluorine [73] have been investigated in detail. From boron and carbon "artificial" radioelements are obtained as the result of certain of the transformations. These are considered more fully in the appropriate section of this report. Lithium has been studied in the form of its separated isotopes,[88] and it has thus been established that the reactions $Li^6 + H^1 \longrightarrow He^4 + He^3$ and $Li^6 + H^2 \longrightarrow Li^7 + H^1$ take place in addition to the three reactions previously known.[51] He^3, hitherto unknown, is also produced in one mode of disintegration of heavy hydrogen by deuterons, $H^2 + H^2 \longrightarrow He^3 + n^1$; the alternative mode, in this case, resulting in the production of a third species of hydrogen, $H^2 + H^2 \longrightarrow H^3 + H^1$.[68] It is very probable that these isobaric nuclei, H^3 and He^3, are both stable.[3, 74] With beryllium no single reaction is established with certainty, but it is known that neutrons are emitted under bombardment with deuterons.[64, 75] The disintegrations produced by deuterons on boron are of great complexity; $B^{10} + H^2 \longrightarrow 3He^4$ and $B^{10} + H^2 \longrightarrow B^{11} + H^1$ are established,[76] and neutrons are also emitted. It is now clear that the corresponding proton-produced disintegration shows unusual features.[77] The suggestion has been made [78] that $B^{11} + H^1 \longrightarrow Be^8 + He^4$ is an occasional mode. Under deuteron bombardment, carbon of mass 12 changes to the next heavier isotope, protons of a single energy being emitted.[76] α-Particles of a single energy are produced when fluorine is bombarded by protons,[79] $F^{19} + H^1 \longrightarrow O^{16} + He^4$.

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[67] *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **3**, 230; *A.*, 1152.

[68] M. L. E. Oliphant, P. Harteck, and (Lord) Rutherford, *Nature*, 1934, **133**, 413; *Proc. Roy. Soc.*, 1934, [*A*], **144**, 692; *A.*, 471, 826; P. I. Dee, *Nature*, 1934, **133**, 564; *A.*, 580.

[69] F. Kirchner, *Sitzungsber. bayr. Akad. Wiss.*, 1933, 129; *A.*, 1934, 128; K. Diebner and G. Hoffmann, *Naturwiss.*, 1934, **22**, 119; *A.*, 342; M. L. E. Oliphant, E. S. Shire, and B. M. Crowther, ref. (88); F. Kirchner and H. Neuert, *Physikal. Z.*, 1934, **35**, 292; *A.*, 471; C. C. Lauritsen and H. R. Crane, *Physical Rev.*, 1934, [ii], **45**, 63; H. R. Crane, C. C. Lauritsen, and A. Soltan, *loc. cit.*, ref. (54); J. D. Cockcroft and E. T. S. Walton, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 704; *A.*, 826; A. Eckardt, R. Gebauer, and H. R. von Traubenberg, *Z. Physik*, 1934, **89**, 582; *A.*, 938; H. R. Crane, L. A. Delsasso, W. A. Fowler, and C. C. Lauritsen, *Physical Rev.*, 1934, [ii], **46**, 531.

[70] H. R. Crane and C. C. Lauritsen, *ibid.*, **45**, 226, 493; H. R. Crane, C. C. Lauritsen, and A. Soltan, *loc. cit.*

[71] F. Kirchner and H. Neuert, *Physikal. Z.*, 1933, **34**, 897; *A.*, 128; also *loc. cit.*, ref. (69); F. Kirchner, *loc. cit.*, and *Naturwiss.*, 1934, **22**, 480; *A.*, 938; C. C. Lauritsen and H. R. Crane, *Physical Rev.*, 1934, [ii], **45**, 493; L. Kurtschatov, G. Schtschepkin, A. Vibe, and V. Bernaschevski, *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **1**, 486; *A.*, 579; J. D. Cockcroft and E. T. S. Walton, *loc. cit.*

[72] C. C. Lauritsen and H. R. Crane, *Physical Rev.*, 1934, [ii], **45**, 345; J. D. Cockcroft and E. T. S. Walton, *loc. cit.*

[73] M. C. Henderson, M. S. Livingston, and E. O. Lawrence, *Physical Rev.*, 1934, [ii], **46**, 38; *A.*, 938; E. McMillan, *ibid.*, pp. 325, 868; H. R. Crane, L. A. Delsasso, W. A. Fowler, and C. C. Lauritsen, *loc. cit.*

[74] See W. W. Lozier, P. T. Smith, W. Bleakney, G. P. Harnwell, and H. D. Smyth, *Physical Rev.*, 1934, [ii], **46**, 81.

Eventually, from a detailed study of these and similar transformations it will obviously be possible to obtain values for the masses of the initial and product nuclei based entirely upon the determined masses of H^1, H^2, He^4, the standard mass O^{16} and the energy changes observed, so long as the usual conservation laws are assumed. At present the masses obtained in this way are to some extent suspect, and no useful purpose will be served by giving a complete list. The "observed" energy changes require in many cases an accurate knowledge of the rate of loss of energy of fast protons and α-particles in mica, and until this is obtained the data must await a final inter-comparison. It is probable, however, that the nuclear mass of He^3 is some 0·0006 ± 0·0004 unit greater than that of H^3, a result just consistent with the stability of both species. The nuclear binding energies, for structures composed of protons and neutrons, are approximately 7 and 8 million electron-volts, respectively. The mass of F^{19} seems likely to be about 0·003 unit higher than F. W. Aston's value.[80]

The experiments of H. R. Crane, C. C. Lauritsen, and their colleagues [81] are concerned with the γ-rays which are emitted in many disintegrations. The following is a summary of their results :

Projectile.	Target.	γ-Ray energy, e.v. × 10^{-6}.	Projectile.	Target.	γ-Ray energy, e.v. × 10^{-6}.
H^1	Li	4 and 12	H^2	C	3·2
H^2	Be	0·7	H^1	F	5·4
H^2	B	$\sim$ 2 and higher			

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[75] H. R. Crane, C. C. Lauritsen, and A. Soltan, *Physical Rev.*, 1934, [ii], **45**, 507; *A.*, 714.

[76] J. D. Cockcroft and E. T. S. Walton, *loc. cit.*, ref. (69).

[77] F. Kirchner and H. Neuert, *loc. cit.*, ref. (69).

[78] F. Kirchner, *Naturwiss.*, 1934, **22**, 480; *A.*, 938.

[79] M. C. Henderson, M. S. Livingston, and E. O. Lawrence, *loc. cit.*

[80] *Proc. Roy. Soc.*, 1927, [*A*], **115**, 487; *A.*, 1927, 914.

[81] *Loc. cit.*, refs. (69)—(73).

Although it is not possible in every case to fix the transformation in which the γ-rays arise, yet it is noteworthy that certain product nuclei may be formed in a number of ways; for instance, B^{11} results from the reactions $N^{14} + n^1 \longrightarrow B^{11} + He^4$ and $B^{10} + H^2 \longrightarrow B^{11} + H^1$; C^{13} from $B^{10} + He^4 \longrightarrow C^{13} + H^1$, $O^{16} + n^1 \longrightarrow C^{13} + He^4$, and $C^{12} + H^2 \longrightarrow C^{13} + H^1$. There is some evidence that the excited states and the subsequent γ-ray emission from such nuclei are independent of the method of their production. Recent information concerning the γ-rays accompanying disintegrations produced by α-particles is due to P. Savel.[82]

II. *The Production of Unstable Species.—α-Particles.* Evidence that high-energy electrons may be associated with the emission of heavy particles in artificial disintegration was first obtained by (Mme.) I. Curie and F. Joliot.[83] It was shown that both positive and negative electrons were emitted from thin layers of beryllium, boron, and aluminium bombarded by the α-particles from polonium. From certain differences observed, it appeared that the phenomenon in the case of beryllium was not of the same nature as with the other two elements. The positrons from boron and aluminium were ascribed to nuclear processes. Both neutrons and protons were known to be emitted from these substances under α-particle bombardment, and the hypothesis was advanced that the emission of a proton, and of a neutron together with a positron, were alternative modes of disintegration. The important discovery was then made [84] that the emission of positrons did not cease with the removal of the α-particle source but continued, decreasing in intensity following an exponential law of decay. Similarly, the positron activity during irradiation rose from zero initially to a limiting value. It was obvious that neutron and positron could not be emitted simultaneously; it was suggested that in all cases a finite time intervened. The observations indicated that an unstable species resulted from the initial disintegration in which neutrons were emitted, and that this species then behaved precisely as a radioelement of short life, the spontaneous emission, however, being of positrons rather than of electrons or α-particles. " Artificial " radioelements with characteristic half-value periods were obtained following the disintegrations of boron, magnesium, and aluminium. Unstable species N^{13}, Si^{27}, P^{30} were postulated, confirmatory chemical evidence being obtained for N^{13} and P^{30}.[85] As an example of the schemes proposed, that representing the sequence of disintegrations produced by α-particles bombarding aluminium may be given in full.

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[82] *Loc. cit.*, refs. (53)—(60).

[83] *Ann. Reports*, 1933, **30**, 354.

[84] (Mme.) I. Curie and F. Joliot, *Compt. rend.*, 1934, **198**, 254; *A.*, 234.

[85] *Idem, ibid.*, p. 559; *Nature*, 1934, **133**, 201; *J. Phys. Radium*, 1934, [vii], **5**, 153; *A.*, 343, 470, 713.

$$\begin{tikzcd}[row sep=small] & \mathrm{Si}^{30} + \mathrm{H}^{1} & \\ \mathrm{Al}^{27} + \mathrm{He}^{4} \arrow[ur] \arrow[dr] & & \\ & \mathrm{P}^{30} + n^{1} \arrow[r] & \mathrm{Si}^{30} + \text{ə} + n^{1} \end{tikzcd}$$

The branching ratio for the primary disintegration is about 20 : 1 in favour of the emission of a proton, and the half-value period for positron (ə) emission is 3·2 ± 0·1 min.[86] It will be noted that the stable end-product along each branch is the same.

The original discovery of positron activity was rapidly confirmed; the activity resulting from boron and aluminium disintegrations was observed by (Frl.) L. Meitner,[87] that from all three elements by C. D. Ellis and W. J. Henderson.[88] New activities following the disintegrations of nitrogen,[89] sodium,[90] phosphorus,[90] and potassium [91] have since been reported. The activity obtained when magnesium is bombarded by α-particles has been shown to be complex,[92] positron activity being attributed to Si^{27}, as above, and negative electron activity to Al^{28}. The latter activity is the more intense. Al^{28} is formed from Mg^{25}, and Si^{27} from Mg^{24}, protons and neutrons being emitted in the respective primary disintegrations. The energy spectrum of the positrons from P^{30} has been investigated by (Frl.) L. Meitner,[93] C. D. Ellis and W. J. Henderson,[86] and A. J. Alichanov, A. J. Alichanian, and B. S. Dželepov.[94] The last authors have also investigated the corresponding spectra for

TABLE V.

	Radio-element.	τ (min.).
Positron-active	N^{13}	14 ± 1
	F^{17}	1·1 ± 0·1
	Al^{26}	0·12 ± 0·02
	Si^{27}	?
	P^{30}	3·2 ± 0·1
	Cl^{34}	40 ± 5
	$\mathrm{Sc}^{42\ (44)}$	180
Electron-active	Al^{28}	2·1 ± 0·2

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[86] C. D. Ellis and W. J. Henderson, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 206; *A.*, 1151.

[87] *Naturwiss.*, 1934, **22**, 172; *A.*, 471.

[88] *Nature*, 1934, **133**, 530; *A.*, 579.

[89] L. Wertenstein, *ibid.*, p. 564; *A.*, 579.

[90] O. R. Frisch, *ibid.*, p. 721; *A.*, 714.

[91] M. Żyw, *ibid.*, **134**, 64; *A.*, 939.

[92] (Mme.) I. Curie and F. Joliot, *J. Phys. Radium*, 1934, [vii], **5**, 153; *A.*, 713; A. J. Alichanov, A. J. Alichanian, and B. S. Dželepov, *Nature*, 1934, **133**, 871; *A.*, 826.

[93] *Naturwiss.*, 1934, **22**, 388; *A.*, 825.

[94] *Nature*, 1934, **134**, 254; *A.*, 1054.

N^{13} and Al^{28} (electrons).[95, 92] At present all these results are not entirely concordant. A provisional list of unstable species and half-value periods (τ) is given in Table V.

Neutrons. The occurrence of unstable species resulting from neutron-produced disintegrations was first noted by E. Fermi,[96] using a strong source of radon-beryllium with fluorine (CaF_2) and aluminium as target elements. Previously, the disintegration of fluorine by neutrons had been investigated by W. D. Harkins, D. M. Gans, and H. W. Newson,[97] the production of an unknown species of nitrogen, N^{16}, being regarded as probable. The suggestion was made that this nucleus might possibly be transformed into O^{16} by emission of a β-particle. Fermi concluded that this, in fact, was the case. He found that the half-value period for the β-particle transformation was about 10 secs. Together with his collaborators, Fermi has rapidly extended these results.[98] More than 60 elements have been bombarded, and definite evidence for subsequent activity has been obtained with more than 40 of them. That the emission of negative electrons is responsible for the greater part of this activity has been directly proved in 12 cases. Since the rest of the data may be explained almost without exception on this assumption, it has been tentatively adopted throughout the work.

From the nature of the case, the data obtained refer more particularly to the characteristics of the activity produced than to the primary disintegrations which give rise to the radioactive species. So far, it has not been possible to make cloud-chamber studies of the primary disintegrations; only chemical methods are available. These methods have shown that the activity after neutron bombardment may be possessed by an element two places or one place removed in the periodic table from the element bombarded—or, sometimes, by an unstable isotope of that element itself. Thus, if the neutron is captured in all transformations, doubly-charged or singly-charged particles or γ-radiation must be emitted. The results to date are satisfactorily explained in terms of α-particles, protons, or quanta as the primary disintegration products, the only difficulty being of a theoretical nature—that of explaining the apparently high probability of simple capture of the neutron by a heavy nucleus. The remaining types of primary

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[95] *Nature*, 1934, **133**, 950; *A.*, 939. [96] *La Ricerca Scient.*, 1934, **5**, (1), 283.

[97] *Physical Rev.*, 1933, [ii], **44**, 945.

[98] See E. Fermi, E. Amaldi, O. D'Agostino, F. Rasetti, and E. Segrè, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 483; E. Fermi, *Nuovo Cim.*, 1934, **11**, 429; E. Amaldi, E. Fermi, F. Rasetti, and E. Segrè, *ibid.*, p. 442; E. Amaldi and E. Segrè, *ibid.*, p. 452, where references to a series of preliminary reports (*A.*, 714, 826) are given.

disintegration become rapidly less probable as the atomic number of the bombarded nucleus increases, as theory predicts, but transformation by pure capture would appear to retain a high probability for all elements. It has been suggested, alternatively, that the transformations observed with heavy elements are non-capture disintegrations resulting in neutron emission, but this hypothesis is not really satisfactory, and it fails definitely in view of the recent discovery [65] that the disintegrations in question become enormously more probable as the kinetic energy of the neutrons is reduced almost to "thermal" values. In the wealth of the data obtained, many cases are indicated of nuclei which are transformed in two or more ways under neutron bombardment and, conversely, several instances in which the same unstable species is the result of more than one primary disintegration. For example, Al^{27} disintegrates in three ways and Al^{28} is formed in three disintegration processes. Thus the decay of activity when certain (pure) targets are activated may be extremely complex. The observations with activated uranium and thorium targets suggest that part of this complexity, in certain cases, must be ascribed to the production of unstable species from which series of successive products arise. From a study of the chemical properties of the products from uranium, E. Fermi [99] concluded that unstable species may occur with $Z > 92$, but a critical examination of the evidence by A. V. Grosse and M. S. Agruss [1] does not support this conclusion.

The extensive investigations carried out in Rome have been followed up in many other laboratories, but no additional discovery of any fundamental importance has been reported. (Mme.) I. Curie, F. Joliot, and P. Preiswerk [2] and R. Fleischmann [3] early discovered that with some elements γ-rays as well as β-particles are emitted during the decay of activity. That this is frequently the case has since been shown by E. Fermi and his collaborators. Confirmation of a large number of results has been obtained by T. Bjerge and C. H. Westcott,[4] and a preliminary investigation made of the results of varying the mean energy of the neutrons employed. M. S. Livingston, M. C. Henderson, and E. O. Lawrence,[5] using "artificially" produced neutrons exclusively, have studied a number of elements, whilst other investigations have been carried out by B. Kurtschatov, I. Kurtschatov, G. Schtschepkin, A. Vibe, and

[99] *Nature*, 1934, **133**, 898; *A.*, 826.
[1] *Ibid.*, **134**, 773; *A.*, 1935, 7.
[2] *Compt. rend.*, 1934, **198**, 2089; *A.*, 826.
[3] *Naturwiss.*, 1934, **22**, 434; *A.*, 938.
[4] *Nature*, 1934, **134**, 177, 286; *A.*, 939, 1054.
[5] *Proc. Nat. Acad. Sci.*, 1934, **20**, 470; *A.*, 1151.

L. Misovski[6] and J. R. Dunning and G. B. Pegram.[7] L. Szilard and T. A. Chalmers[8] have introduced an ingenious method of concentrating the activity when the unstable species is isotopic with its parent substance.

Finally, it may be remarked that, whilst certain neutron-produced disintegrations are set in evidence through the radioactivity of the products of transformation, it is to be expected that many other disintegrations must occur without being recognised in this way. The investigation of the primary disintegrations of complex heavy elements will obviously be complicated by this fact.

Protons and deuterons. The observations of J. D. Cockcroft, C. W. Gilbert, and E. T. S. Walton[9] and C. C. Lauritsen, H. R. Crane, and W. W. Harper[10] provided the first evidence for the production of unstable species by bombardment with protons and deuterons, respectively. The former authors established the emission of positrons from carbon bombarded by protons; the latter a similar emission from a number of light elements subjected to deuteron bombardment. The effect has since been reported upon by M. C. Henderson, M. S. Livingston, and E. O. Lawrence,[11] C. C. Lauritsen and H. R. Crane,[12] and S. H. Neddermeyer and C. D. Anderson.[13] At present, carbon is the only element the activation of which by proton bombardment is proved beyond doubt. No recoil phenomena have been observed in the primary transformation and this and other evidence point to the formation of N^{13} by simple capture of the proton. Bombardment by deuterons, as above described (p. 388), with many elements results in the emission of protons and the transformation of one stable isotope into the (stable) isotope of next higher mass number. This emission of a proton may sometimes be replaced by the successive ejection of neutron and positron; when this occurs the intermediate species is unstable, as when α-particles are responsible for the disintegration (see above). With deuterons, as with α-particles, the branching ratio is large, in favour of proton emission. If all the results which have been reported are substantially correct, then the yield of active product must frequently depend very considerably upon the energy of the deuterons employed. There is, however, general agreement that N^{13}, of half-value period 11 ± 1 mins., and C^{11}, of period about 20 mins., result from the activation of carbon and boron, respectively. The problem of the identity, or otherwise, of the N^{13} thus formed and the active product from boron bombarded by α-particles (p. 389) awaits solution.

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[6] *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **3**, 221, 226; *A.*, 1152.

[7] *Physical Rev.*, 1934, [ii], **45**, 768.

[8] *Nature*, 1934, **134**, 462; *A.*, 1152.

[9] *Ibid.*, **133**, 328; *A.*, 342.

[10] *Science*, 1934, **79**, 234; *A.*, 579.

[11] *Physical Rev.*, 1934, [ii], **45**, 428.

[12] *Ibid.*, pp. 430, 497.

[13] *Ibid.*, pp. 498, 653.

The Theory of β-Particle Disintegration.

The successful application of the principles of wave-mechanics to the explanation of the main features of the α-particle disintegration was one of the early and most striking achievements of this new method of theoretical approach.[14] Very few special assumptions were needed, and progress in this and in the analogous explanation of artificial disintegration was relatively rapid. At the present stage of development, further investigation is unlikely to add materially to the accepted theory,[15] and the centre of interest has shifted to the formulation of a satisfactory theoretical treatment of the β-disintegration. Here no progress is possible without particular assumptions.

The form which these assumptions were to take was determined by several considerations. The discovery of the neutron of mass number 1 [16] made it possible—if this were significant—to regard all nuclei as built up of particles known to exist in the free state, without requiring for this purpose the presence of electrons in the nuclear structure. Existing theory was then, and still is, incapable of describing the behaviour of particles of so small a mass within so restricted a region of space. Next, the relation discovered by B. W. Sargent [32] and the apparently successful *ad hoc* hypotheses put forward by C. D. Ellis and N. F. Mott [40] redirected attention towards the maximum β-particle energy as the important parameter in terms of which to work. Furthermore, there was another such hypothesis, due to W. Pauli,[17] of earlier date. This postulated the emission of a second particle (neutrino), having no charge and very small mass, in β-disintegration; the sum of the kinetic energies of electron and neutrino being constant for all β-transformations between the same initial and final nuclei. Finally, the discovery of electron and positron emission from unstable species of widely different atomic number (artificial radioactivity) provided new data and a qualitatively distinct phenomenon (positron activity) which any successful theory was obliged to explain.

These considerations lead naturally to the theory of E. Fermi.[18]

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[14] *Ann. Reports*, 1930, **27**, 317.

[15] See H. Casimir, *Physica*, 1934, **1**, 193; *A.*, 234; T. Sexl, *Z. Physik*, 1933, **87**, 105; *A.*, 127.

[16] *Ann. Reports*, 1932, **29**, 305.

[17] See J. F. Carlson and J. R. Oppenheimer, *Physical Rev.*, 1931, [ii], **38**, 1787.

[18] *Z. Physik*, 1934, **88**, 161; **89**, 522; *A.*, 579, 827.

His was not, however, the first attempt at a detailed treatment of the problem; it is given priority here merely for convenience of presentation. The theory developed by G. Beck [19] derives less from the point of view above expressed; it will be considered further in what follows. These two theories and other work up to date have been discussed by G. Gamow.[20] Fermi bases his theory on the nuclear model proposed and developed by W. Heisenberg.[21] For this model, the sole constituent particles are protons and neutrons, and these two, Fermi regards as different inner quantum states of a single "particle." A quantum jump between the two states results in the creation of an electron or a positron according as the initial state of the "particle" was neutron or proton state. A neutrino or antineutrino is simultaneously created, and the pair of particles, electron and neutrino, or positron and antineutrino, are ejected from the nucleus, sharing between them the available energy. The probability of such a jump, and so the decay constant for β-disintegration, depends very notably on the difference in angular momentum between initial and final nuclei. The probability is greatest when there is no change in this quantity. From this point of view, those radioelements to which the upper of Sargent's two curves is appropriate suffer β-disintegration generally without change of nuclear spin (permitted transitions); in other β-transformations this change is not usually zero (forbidden transitions). G. Gamow [37] has attempted to develop this conclusion and assign spin values to the normal and certain excited states of the nuclei of successive elements in the thorium series.

The neutrino hypothesis was introduced in order to make possible an explanation of a continuous distribution of energy amongst the β-particles from a given product without violation of the conservation laws. The more detailed evaluation of the particular type of continuous distribution which is found obviously requires more precise assumptions concerning the mass of the neutrino. If these assumptions run counter to established data, the hypothesis necessarily fails. Fermi has shown that the form of the distribution near the high-energy limit is sensitive to the assigned mass, whilst a similar sensitivity of the position of the maximum has been deduced by F. Perrin.[22] Both authors conclude that the rest mass of the particle is most probably zero. No immediate contradiction is involved in such a conclusion. On Fermi's theory, the form of the continuous spectrum depends also on the change of nuclear angular momentum in the disintegration. General differences in form as between the continuous spectra corresponding to permitted and forbidden transitions had previously been noticed by C. D. Ellis and N. F. Mott.[40] These differences are qualitatively of the type which theory predicts. The application of the theory to the case of positron emission has been worked out by G. C. Wick.[23] Discrepancies indicate its present imperfections. Criticisms have also been advanced by I. Tamm [24] and discussed by D. Iwanenko.[25]

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[19] *Z. Physik*, 1933, **83**, 498; **84**, 811; *A.*, 1933, 884, 995; G. Beck and K. Sitte, *ibid.*, 1933, **86**, 105; *A.*, 1933, 1224; 1934, **89**, 259; *A.*, 826; *Nature*, 1934, **133**, 722; *A.*, 713.

[20] *Physikal. Z.*, 1934, **35**, 533; *A.*, 827.

[21] *Z. Physik*, 1932, **77**, 1; **78**, 156; *A.*, 1932, 894, 1074; *ibid.*, 1933, **80**, 587; *A.*, 1933, 335.

[22] *Compt. rend.*, 1933, **197**, 1625; **198**, 2086; *A.*, 127, 827.

The theory of G. Beck is based on different assumptions. For him, inability to treat theoretically the binding of electrons in nuclei is simply evidence for the present inadequacy of the theory; it does not follow from this inability—which cannot be proved to be permanent—that electrons do not exist as nuclear particles. He assumes, in fact, a structure composed of α-particles, not more than three protons and "free charges." The latter are electrons which, within the nucleus, retain only their charge and symmetry properties. In β-disintegration there is instability in this system of charges, with the result that the net positive charge on the nucleus has to be increased (or, in positron disintegration, decreased) by one unit. Materialisation of energy occurs, as in other known cases, by the creation of a pair of electrons, positive and negative. Only one of these electrons escapes from the nucleus.[26] The capture of the other takes place, in a manner which present theory is unable to describe, so that only the charge of the particle is retained by the nucleus. Its energy is lost to observation. The feature of β-disintegration which on Fermi's theory is described in terms of the emission of an unobserved particle, the neutrino, is here represented by this process of capture of the second particle with the loss of its purely mechanical attributes. No attempt is made to save the conservation laws of macroscopic physics. This procedure may be characterised by the greater intellectual integrity: it does not on that account alone make for the more successful theory. Since both the above theories treat the disintegration as a double process, and on each, the disintegration probability depends markedly on the change in angular momentum, it will not be easy to decide experimentally between their conclusions until all arbitrary constants are replaced by quantities which are theoretically derived.

Experimental proof of the emission of neutrinos would, of course, settle the question, but it is very unlikely that these particles will be easily observed.[27] J. Chadwick and D. E. Lea [28] have shown that, if they are in fact emitted in the disintegration of radium-*E*, then the ionisation which they produce corresponds to less than one ion-pair in 150 km. of standard air. From the theoretical viewpoint, the idea of a neutrino with objective existence appears to have had some attraction. L. de Broglie,[29] J. L. Destouches,[30] A. Proca,[31] and B. Kwal [32] have attempted to develop a theory of the propagation of photons in which neutrino and antineutrino have a natural significance.

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[23] *Atti R. Accad. Lincei*, 1934, [vi], **19**, 319; *A.*, 713.

[24] *Nature*, 1934, **133**, 981; *A.*, 827.

[25] *Ibid.*, p. 981; *A.*, 827.

[26] A suggestion of this type has also been made by M. N. Saha and D. S. Kothari, *ibid.*, 1933, **132**, 747; 1934, **133**, 99; *A.*, 235.

Anomalous Absorption of Hard γ-Rays : the Positive Electron.

The discovery of the positive electron occurred during the period covered by the last report.[33] As there described, this new particle was found, first of all, as one component of the penetrating radiation at sea-level. It was then established that it might be produced by the action of high-energy γ-radiation on matter, in which mode of production a pair of electrons, one positive and one negative, was invariably associated with the disappearance of a quantum of radiation. Now, such a mode of interaction between radiation and matter had not until then been considered by experimentalists. There was in existence, however, a theory due to P. A. M. Dirac [34] which provided a natural way of regarding the simultaneous appearance of pairs of electrons of, apparently, opposite sign of charge, and this at once provided a basis for theoretical calculations concerning the probability of the production of such pairs at the expense of the quantum energy of electromagnetic radiation. There was also in existence considerable experimental evidence [35] to show that in the absorption of high-energy γ-rays, more particularly by substances of high atomic weight, processes were involved which at the time had no theoretical explanation. The electronic absorption coefficient[36] for γ-rays of $2{\cdot}6 \times 10^6$ e.v. energy was in excess of the sum of the coefficients for photoelectric absorption and Compton scattering by an amount which appeared to vary directly as the atomic number of the scattering element, and to reach roughly 20% of the total when that element was lead. Recently, sources of artificially-produced γ-rays of still higher energy have become available (see above), and with one of these E. McMillan[73] has shown that, for radiation of $5{\cdot}4 \times 10^6$ e.v. energy, approximately 60% of the absorption in lead is "excess" absorption, whilst at this energy, also, μ_e varies linearly with atomic number. H. R. Crane, L. A. Delsasso, W. A. Fowler, and C. C. Lauritsen[69] have extended the measurements to 12×10^6 e.v.[37] Here the additional absorption in lead is nearly 10 times as great as that due to scattering by extranuclear electrons. In this energy range (1—12×10^6 e.v.), therefore, the absorption coefficient in lead is not a continuously decreasing function of increasing quantum energy, as had previously been supposed. γ-Rays of about 3×10^6 e.v. energy are more penetrating (in lead) than radiations of either greater or less quantum energy. Failure to appreciate this fact has doubtless been responsible for inconsistencies in the past: certainly, it renders completely worthless any estimation of wave-length from absorption measurements by simple extrapolation of the Klein–Nishina formula beyond the range of radioactive γ-ray energies.

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[27] H. Bethe and R. Peierls, *Nature*, 1934, **133**, 532, 689; *A.*, 580, 714.

[28] *Proc. Camb. Phil. Soc.*, 1934, **30**, 59.

[29] *Compt. rend.*, 1934, **198**, 135; *A.*, 236.

[30] *Ibid.*, p. 467; *A.*, 342.

[31] *Ibid.*, p. 643; *A.*, 343; *J. Phys. Radium*, 1934, [vii], **5**, 157; *A.*, 715.

[32] *Compt. rend.*, 1934, **199**, 23; *A.*, 939.

[33] *Ann. Reports*, 1933, **30**, 355.

[34] See *Ann. Reports*, 1930, **27**, 325.

[35] G. T. P. Tarrant, *Proc. Roy. Soc.*, 1930, [*A*], **128**, 345; *A.*, 1930, 1085; 1932, [*A*], **135**, 223; *A.*, 1932, 318; C. Y. Chao, *Proc. Nat. Acad. Sci.*, 1930, **16**, 431; *A.*, 1930, 1086; *Physical Rev.*, 1930, [ii], **36**, 1519; *A.*, 1931, 142; *Proc. Roy. Soc.*, 1932, [*A*], **135**, 206; *A.*, 1932, 318; (Frl.) L. Meitner and H. H. Hupfeld, *Z. Physik*, 1931, **67**, 147; *A.*, 1931, 281; J. C. Jacobsen, *ibid.*, 1931, **70**, 145; *A.*, 1931, 995.

Now, calculations concerning the excess absorption by pair-production early led to the result that the effective cross section per nucleus must vary as the square of the nuclear charge,[38] *i.e.*, that there must be an "additional" part of μ_e proportional to the atomic number. It became natural, therefore, to ascribe to the production of pairs the observed additional absorption which was found to vary in precisely this way from element to element. Moreover, for the γ-ray of $2{\cdot}6 \times 10^6$ e.v. energy, there was good agreement between experimental and theoretical values for this excess absorption. The calculations have now been extended by Y. Nishina, S. Tomonaga, and S. Sakata[39] and H. Bethe and W.

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[36] The electronic absorption coefficient (μ_e) represents the fractional decrease in intensity, per extranuclear electron per cm.^{2} area of a thin absorbing foil, which occurs when the radiation passes normally through the foil. It is also, numerically, the mean cross-sectional area per electron effective in the process of absorption. The atomic absorption coefficient (μ_a) is defined in a precisely similar manner. It may be regarded, when this point of view is significant, as the target area per atomic nucleus effective in absorption.

[37] The γ-ray energy was determined independently by magnetic analysis of the secondary electrons produced in the course of its absorption.

[38] *Ann. Reports*, 1933, **30**, 358.

[39] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **24**, 1; *A.*, 825.

Heitler,[40] and it is clear that this satisfactory numerical agreement extends over the whole range of investigated energies, say up to 12×10^6 e.v. From these results it might thus be concluded that the production of positron-electron pairs was undoubtedly the mechanism by which the hitherto anomalous absorption was to be completely explained. The extensive cloud-chamber experiments of J. Chadwick, P. M. S. Blackett, and G. P. S. Occhialini [41] entirely support this conclusion.

Most of the experiments on anomalous absorption, however, have been concerned with an analysis of the radiation, other than Compton scattered γ-radiation, which is re-radiated by a target irradiated by γ-rays—either the approximately homogeneous γ-radiation from thorium-C'' ($2{\cdot}6 \times 10^6$ e.v. energy), or the very inhomogeneous radiation from the short-lived products of radon. Here, conclusions are very much less definite. Experiments have recently been performed by (Frl.) L. Meitner and H. Kösters,[42] E. Stahel and E. Ketelaar,[43] T. Heiting,[44] L. H. Gray and G. T. P. Tarrant,[45] and W. Bothe and W. Horn,[46] amongst others. There is now almost complete agreement that from all scatterers a radiation is emitted, roughly isotropically, of about 5×10^5 e.v. energy—whether the primary radiation be that of thorium or of radium active deposit. Its intensity, per atom of the scatterer, is found to vary as the square of the atomic number; for light elements it represents the bulk of the "anomalous" scattering. There is every reason to believe that this component of the scattered radiation arises in the annihilation of positive electrons which have lost almost all their original kinetic energy. Qualitatively, this is entirely in agreement with the hypothesis which has been made concerning the nature of the anomalous absorption. At some stage, the positive electrons produced in the pairs must suffer annihilation. Theory indicates that, for positrons of the energies concerned, a small proportion only of these annihilation collisions will occur before the energy has been reduced almost to zero. In most cases, then, the annihilation radiation will be expected to consist of quanta of $0{\cdot}51 \times 10^6$ e.v. energy, two equal quanta being emitted for every positron which disappears.

It is rather when the absolute intensity of the radiation is considered that difficulties first arise. There is, however, no real agreement concerning absolute intensities. L. H. Gray and G. T. P. Tarrant [45] find more scattered radiation of about this (annihilation) wave-length than absorption measurements (regarded from the point of view of the theory of pair production) would predict; they suggest, tentatively, the production of double pairs as an explanation, since this would diminish the fraction of the primary energy dissipated as kinetic energy of electrons and positrons. On the other hand, there is at present no direct evidence for the production of more than single pairs by quanta of radioactive energies, although the production of showers in penetrating radiation is generally regarded as essentially the same type of process, many pairs being produced simultaneously when the quantum energy is high.

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[40] *Proc. Roy. Soc.*, 1934, [*A*], **146**, 83; *A.*, 1150.

[41] *Ibid.*, **144**, 235; *A.*, 468.

[42] *Z. Physik*, 1933, **84**, 137; *A.*, 1933, 883.

[43] *J. Phys. Radium*, 1933, [vii], **4**, 460; *A.*, 1933, 1224; 1934, [vii], **5**, 512.

[44] *Naturwiss.*, 1933, **21**, 800; *A.*, 5; *Z. Physik*, 1933, **87**, 127; *A.*, 127.

[45] *Proc. Roy. Soc.*, 1932, [*A*], **136**, 662; *A.*, 1932, 791; 1934, [*A*], **143**, 681, 706; *A.*, 342.

[46] *Naturwiss.*, 1934, **22**, 106; *A.*, 342; *Z. Physik*, 1934, **88**, 683; *A.*, 713.

However, a more fundamental difficulty than that caused by discrepancies in observed and calculated intensities concerns the hard components of the scattered radiation. The single aspect of agreement, here, is that this component varies in intensity, per atom of the scatterer, considerably more rapidly than the square of the atomic number. Even with lead, less than one quantum of the more energetic radiation is emitted for every 10 quanta of the less energetic. (Frl.) L. Meitner and H. Kösters [42] and W. Bothe and W. Horn [46] consider that the hard component is radiation of the same frequency as the primary radiation, but L. H. Gray and G. T. P. Tarrant,[45] T. Heiting,[44] and E. Stahel and E. Ketelaar [43] report differently. None of these authors finds any evidence of appreciable scattering without change of wave-length. Gray and Tarrant estimate a mean energy for the hard component from lead of $1{\cdot}1 \times 10^6$ e.v., whilst both they and Stahel and Ketelaar consider that the results contain nothing contrary to the simplest assumption, *viz.*, that the effective wave-length of the hard component is approximately independent of the scattering material. It is probable that the greatest proportion of this radiation will eventually be found to be annihilation radiation emitted in the annihilation of positrons of considerable kinetic energy. This may occur with the production of a single quantum of radiation, or of two quanta. The probability that one or other of these processes will take place does not vary very markedly with the atomic number of the scattering material, but the partial probability of the former of them is very much greater in heavy scatterers than in light. In scattering substances of low atomic number, the second process will result in unequal quanta, one of energy greater than, and the other of energy less than, $0{\cdot}51 \times 10^6$ e.v. It may be shown that most of the low-energy quanta will have about $0{\cdot}25 \times 10^6$

e.v. energy.[47] It is noteworthy that Gray and Tarrant consider that the mean quantum energy of the soft component of the scattered radiation is in all cases slightly less than 0·5 × 10^6 e.v. At present, there are questions of intensity ratios which must be solved before the above explanation can be accepted, and for this reason, and in an attempt to explain the reported observation of scattered radiation of nearly the primary hardness, other suggestions have been made. For instance, C. C. Lauritsen and J. R. Oppenheimer [48] believe that the production of " white " *X*-radiation in the scattering material by recoil- and photo-electrons is capable of explaining some of the results. The hard component of this radiation would be emitted chiefly in or near the forward direction, and in that direction would have a maximum energy approaching that of the primary radiation. W. Bothe and W. Horn [46] have reported a high-energy hard component of which the emission is highly anisotropic. C. C. Lauritsen and J. R. Oppenheimer [48] conclude that coherent scattering by electrons in negative-energy states near the nucleus cannot be sufficiently intense to be in question here. The affirmative suggestion was made by M. Delbrück [49] who, at the same time, had considered the complementary suggestion that incoherent (Compton) scattering by such electrons might occur, but had concluded that it would not. However, the complete theoretical calculations for these processes have yet to be made. From the experimental side, further advance is likely to come from a study of the scattering from very thin sheets of material. Stahel and Ketelaar [43] and Bothe and Horn [46] have made a beginning in this direction, but the smallest thickness of scatterer used by the former authors was 0·4 g./cm.^{2} (lead) and by the latter authors 0·7 g./cm.^{2} (carbon). Such scatterers already absorb completely a large fraction of the electrons produced in their bulk.

The calculations of H. Bethe and W. Heitler [40] apply to pair production by fast electrons as well as to the process which has just been considered. For equal energies of electron and quantum, it appears that the nuclear cross-section for pair-production is about 137 times greater for a quantum of radiation than it is for an electron. C. D. Anderson, R. A. Millikan, S. H. Neddermeyer, and W. Pickering [50] have obtained a few cloud-chamber photographs showing the production of pairs during the passage of high-energy electrons from the penetrating radiation through a lead plate. The frequency of production appears to be roughly as calculated. D. Skobeltzyn[51] has published a single photograph which is best interpreted as showing the production of a pair by an electron of a few million electron-volts energy whilst traversing the gas in the cloud chamber. Other rare events of a similar nature which might occasionally be observed have been discussed by F. Perrin[52] from a theoretical standpoint.

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[47] H. J. Bhabha and H. R. Hulme, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 723; H. Bethe, unpublished.

[48] *Physical Rev.*, 1934, [ii], **46**, 531.

[49] *Z. Physik*, 1933, **84**, 144.

[50] *Physical Rev.*, 1934, [ii], **45**, 352; *A.*, 580.

Since it has now been established that positron–electron pairs may be produced by the interaction of quanta and of fast electrons with the fields of force surrounding atomic nuclei, and since both quanta and fast electrons are emitted from the nuclei of certain radioactive substances, it is interesting to consider the possibility of "internal-conversion" effects, whereby the emission of pairs may replace the emission of quanta in some instances, or accompany the emission of electrons (of reduced energy) in others. There has been definite evidence for some time[53] that sources of radon, radio-thorium, or thorium-active deposit enclosed in thin-walled glass tubes emit positive as well as negative electrons, and a certain amount of evidence that this effect, of the order of 1% of the total β-particle emission, is to be attributed to the radioactive substance itself. The calculations of L. Nedelsky and J. R. Oppenheimer[54] make it rather unlikely that the chief cause here is internal conversion of γ-radiation. More recent experiments of A. J. Alichanov and M. S. Kosodaev,[55] who used a radon source and magnetic analysis, have provided further data on the subject. From this it seems probable that the appearance of positrons is connected with the nuclear emission of electrons in radioactive β-decay.

The recently-discovered emission of positive electrons from nuclei in "artificial radioactivity" is discussed more fully in another place (p. 389). It remains to remark here that, whilst fairly successful formal theories of this effect have been advanced, their connexion with the original theory of pair-production is not always very apparent. That theory has to describe the materialisation of particles (with conservation of charge) at the expense of kinetic energy or of the energy of electromagnetic radiation; the theory of β-disintegration is concerned with materialisation taking place at the expense of the potential energy of a complex system. If the simple idea of pair-production is retained, it is necessary to postulate a mechanism by which only a single member of the pair is observed outside the nucleus; if it is not retained, then some new assumption must be made. The properties of the positive electron, once it has left the nucleus, are in no way different from those of a positron produced in any other way; its observability must be regarded as dependent upon the continued existence of a vacancy in an electron state of negative energy, whilst its ultimate annihilation is described as the capture of an originally observable (negative) electron into this vacant state. In any self-consistent theory, the initial appearance of this vacancy must eventually be described in terms of the transitions of negative electrons.

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[51] *Nature*, 1934, **133**, 23; *A.*, 127.

[52] *Compt. rend.*, 1933, **197**, 1100, 1302; *A.*, 1934, 6.

[53] J. Thibaud, *Compt. rend.*, 1933, **197**, 915; *A.*, 1934, 4; J. Chadwick, P. M. S. Blackett, and G. P. S. Occhialini, *loc. cit.* (ref. 41); D. Skobeltzyn and E. Stepanowa, *Nature*, 1934, **133**, 565, 646; *A.*, 578.

[54] *Physical Rev.*, 1933, [ii], **44**, 948; 1934, [ii], **45**, 136, 283.

[55] *Z. Physik*, 1934, **90**, 249; *A.*, 1150.

Experiments designed to demonstrate the properties of positive electrons have been carried out by E. J. Williams,[56] using the positrons produced in the "additional" absorption of γ-rays, by J. Thibaud,[57] employing the positrons from a radioactive source, and by F. Joliot,[58] with the positrons emitted by certain artificially produced radioelements. Certain outstanding difficulties in the theory of the positron have been discussed from various viewpoints by V. Fock,[59] W. H. Furry and J. R. Oppenheimer,[60] Y. Nishina and S. Tomonaga,[61] W. Heisenberg,[62] and P. A. M. Dirac.[63]

Various possibilities of interaction between γ-radiation and atomic nuclei have already been discussed, but amongst them no case of interaction specific to any nucleus has so far been considered. The processes involved merely require the existence of very strong electric fields in order to possess appreciable probability; such field intensities are to be found only in the neighbourhood of an atomic nucleus. Very recently, however, two cases of specific interaction have been recorded. J. Chadwick and M. Goldhaber [64] subjected heavy hydrogen gas to the action of the γ-rays from a radiothorium source. They obtained evidence of the liberation of protons with considerable energy. It became obvious that a nuclear photo-effect was in question, the reaction being written $H^2 + W_\gamma = H^1 + n^1 + Q$, W_γ and Q being respectively the γ-ray energy and the sum of the kinetic energies of the liberated particles. This reaction fixes the mass of the neutron as 1·0080 ± 0·0005 on the atomic scale ($O^{16} = 16$). Later, L. Szilard and T. A. Chalmers [65] detected the neutrons produced in the analogous photo-disintegration of beryllium; the γ-rays from radium-active deposit were employed.

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[56] *Nature*, 1934, **133**, 415; *A.*, 470.

[57] *Compt. rend.*, 1933, **197**, 915, 1629; 1934, **198**, 562; *Ann. Soc. sci. Bruxelles*, 1934, [*B*], **54**, 36; *Physical Rev.*, 1934, [ii], **45**, 781; *A.*, 4, 126, 341, 468, 825.

[58] *Compt. rend.*, 1933, **197**, 1622; **198**, 81; *J. Phys. Radium*, 1934, [vii], **5**, 299; *A.*, 126, 236, 1054.

[59] *Compt. rend. Acad. Sci. U.R.S.S.*, 1933, 267; *A.*, 341.

[60] *Physical Rev.*, 1934, [ii], **45**, 245; *A.*, 468; *ibid.*, pp. 343, 903.

[61] *Japan. J. Physics*, 1934, **9**, 85; *A.*, 578.

[62] *Z. Physik*, 1934, **90**, 209; *A.*, 1150.

[63] *Proc. Camb. Phil. Soc.*, 1934, **30**, 150.

[64] *Nature*, 1934, **134**, 237; *A.*, 1053.

The Penetrating Radiation.

The general picture of the character of the penetrating radiation presented in this report last year [66] remains almost unchanged. Electrified particles (the majority probably positive electrons) approach the earth from outer space and, in their passage through the atmosphere, produce secondary and tertiary radiations, partly electronic, partly very probably quantum in character, with many of the electronic tertiaries arising in " showers " of zero net charge.

If, however, there has been little change in this picture, it must not be concluded either that the volume of work on this particular subject is less than formerly or that complete agreement has been reached amongst the many workers in the field. There is at present, for instance, almost complete disagreement concerning a possible neutron component of the radiation. Thus G. L. Locher [67] and L. V. Misovski and M. S. Eigenson [68] have reported affirmatively regarded its presence from cloud-chamber observations, although negative results have been obtained by (Mme.) I. Curie and F. Joliot [69] and E. Regener and R. Auer,[70] using ionisation-chamber methods. Neither is there any real agreement regarding the incidence of high-energy protons, or other heavy charged particles, as possible components of the radiation. W. Kolhörster [71] and A. Corlin,[72] having extended the range of depth observations to the equivalent of about 600 m. of water, still find evidence of some ionisation due to external agents. It has been suggested, *e.g.*, by A. H. Compton and H. Bethe,[73] that high-energy protons alone could possess such extreme penetrating power, coupled with the other observed properties of this radiation. Another suggestion, by A. H. Compton and R. J. Stephenson,[74] directed towards explaining a feature of the high-altitude absorption curves, involves protons or multiply-charged particles of lower energy. This may become

[65] *Nature*, 1934, **134**, 494; *A.*, 1151. [66] *Ann. Reports*, 1933, **30**, 358.

[67] *J. Franklin Inst.*, 1933, **216**, 673; *A.*, 1934, 235.

[68] *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **2**, 221; *A.*, 714.

[69] *J. Phys. Radium*, 1933, [vii], **4**, 492; *A.*, 1933, 1225.

[70] *Physikal. Z.*, 1934, **35**, 784; *A.*, 1152.

[71] *Nature*, 1934, **133**, 419; *A.*, 471; *Z. Physik*, 1934, **88**, 536; *A.*, 580.

[72] *Nature*, 1934, **133**, 63; *A.*, 128.

[73] *Ibid.*, **134**, 734.

[74] *Physical Rev.*, 1934, [ii], **45**, 441; *A.*, 580.

untenable in view of the recent results of E. Regener and G. Pfotzer,[75] who found that the increase in intensity with height up to about 28 km. above sea-level was very closely the same whether the intensity was determined by tube counters or, as has been more usual hitherto, by ionisation chambers. Obviously, a closer comparison of the data from these two methods is desirable. Finally, there is considerable difference of opinion concerning the amount and quality of any quantum radiation which may enter at the top of the atmosphere along with the particle radiation which has already been assumed. Moreover, opinions upon this question will obviously influence the status assigned to the electronic showers—whether these be considered as tertiary or secondary phenomena. After these preliminary comparisons, the year's experiments may now be reviewed somewhat more systematically.

The most direct information is obtained from cloud-chamber photographs taken in strong magnetic fields. Here, C. D. Anderson, R. A. Millikan, S. H. Neddermeyer and W. Pickering [50] have extended the earlier results of Anderson. At sea-level, individual electrons and, more particularly, positrons, may have energies certainly up to 5×10^9 e.v.; electrons and positrons occurring in showers have smaller energies. The maximum total energy of the particles in a single shower has not so far exceeded the limit observed for single particles. Many instances of showers produced in material screens contained in the cloud chamber have been found, the majority of them having obviously been produced by some non-ionising radiation. Large numbers of low-energy electrons and pairs produced both in the screens and in the gas filling the chamber are almost conclusive proof of the occurrence of quanta of about 10^7 e.v. energy simultaneously with the showers. It is presumed that the non-ionising radiation of higher energy is also quantum in character. By evaluating, from observed track curvatures, the loss of energy of electrons traversing screens of carbon and lead, large random losses are established—chiefly in lead. The evidence supports the view that a quantum radiation is emitted.

Less direct evidence concerning the shower-producing radiation is obtained from observations with several tube counters. First, however, it should be mentioned that the use of two widely separated counters with interposed absorption screens of variable thickness allows of an analysis of the corpuscular radiation at any place in respect of its penetrating power—an analysis only one stage less direct than that in respect of magnetic deflectability, provided by the counter-controlled expansion chamber operated in a magnetic field. Following W. Bothe and W. Kolhörster,[76] B. Rossi[77] has been the chief exponent of this method. Together with G. Bottecchia,[78] he has completely established the validity of the method, held to be suspect, at one time, by R. A. Millikan.[79] Rossi[80] also was the first to employ three counters in a study of showers and the shower-producing radiation. Recently, this arrangement has been very widely used. E. Fünfer,[81] J. H. Sawyer,[82] C. W. Gilbert,[83] and G. Alocco and A. Drigo[84] have obtained results here in which there is a large measure of agreement. These experiments show, first, that, for any locality, the shower particles produced in a given substance are for the most part fairly homogeneous with respect to energy (C. W. Gilbert[83] finds that this characteristic energy increases from about 7×10^7 e.v. to 10^8 e.v. from sea-level to about 3·5 km. altitude), and, secondly, that the absorption of the main shower-producing radiation, particularly in heavy elements, is very much more rapid than that of the primary penetrating radiation. The atomic absorption coefficient for the latter varies roughly as the atomic number of the absorbing material;[85] for the former this coefficient,[83] as well as the target area of the nucleus effective in shower production,[84] appears to vary as the square of the atomic number. Shower production, therefore, seems to be the principal mode in which the so-called shower-producing radiation interacts with matter. The linear absorption coefficient in lead for the shower-producing radiation at sea-level is about 0·35 cm.$^{-1}$. It may be noted that this is not many times smaller than the calculated limiting value,[40] for high quantum energies, of the coefficient for pair-production by nuclear interaction of electromagnetic radiation. Moreover, the dependence of absorption coefficient upon atomic number is seen to be the same for pair-production by relatively low-energy quanta as it is for shower production by the radiation which is responsible for the showers. Thus, all the evidence suggests that this radiation is, in fact, high-energy quantum radiation; similarly it indicates that present theory is inadequate fully to describe the absorption processes, although obviously possessing a measure of truth. If the shower-producing radiation be secondary to the primary corpuscular radiation, then the different dependence of their absorption coefficients upon atomic number requires that the equilibrium ratio of secondary to primary radiation should be greatest for substances of low atomic weight. The three-counter absorption curves are consistently explained on this assumption. From experiments with ionisation chambers, H. Schindler[86] had already concluded that transition effects occur when the radiation passes from one medium to another, and that these may be explained in terms of the readjustment of equilibrium ratios between primary and secondary radiations. It is probable that the two sets of experiments provide evidence for one and the same phenomenon.

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[75] *Physikal. Z.*, 1934, **35**, 779; *A.*, 1152.

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[76] *Ann. Reports*, 1930, **27**, 322.

[77] *Z. Physik*, 1933, **82**, 151; *Physical Rev.*, 1934, [ii], **45**, 212.

[78] *La Ricerca Scient.*, 1934, **5**, (1), 171.

[79] *Physical Rev.*, 1933, [ii], **43**, 661.

[80] *Physikal. Z.*, 1932, **33**, 304.

[81] *Z. Physik*, 1933, **83**, 92.

[82] *Physical Rev.*, 1933, [ii], **44**, 241; *A.*, 1933, 996.

[83] *Proc. Roy. Soc.*, 1934, [*A*], **144**, 559; *A.*, 827.

[84] *La Ricerca Scient.*, 1934, **5**, (1), 112.

[85] Since the ratio of atomic number to mass number does not differ much from one atom to another, this dependence of μ_a on Z expresses the fact that the mass absorption coefficient is approximately the same for all substances.

There remains one feature of the ionisation due to the penetrating radiation which it is possible to investigate only in ionisation chambers of large gas capacity. This is the phenomenon of ionisation bursts or "Stösse."[87] These bursts have been investigated by E. G. Steinke and H. Schindler[88] and by W. Messerschmidt,[89] amongst others. Amounts of energy are involved of the same order of magnitude as that released in the showers, but its dissipation as ionisation occurs in a much smaller volume than is possible for the most complex shower so far observed. It is very unlikely, therefore, that "showers" and "bursts" are of the same essential character. The frequency and size of the bursts in a given chamber depend markedly upon the nature and thickness of the material immediately surrounding the chamber. Information concerning the identity of the burst-producing radiation will no doubt be obtained by a closer study of this dependence. It seems already improbable that the primary corpuscular radiation is the immediate agent.

The question of the time dependence of the intensity of the penetrating radiation has received further elucidation by W. Messerschmidt.[90] The greater part, at least, of a small apparent fluctuation in the intensity of the unfiltered radiation with a period of a solar day is traced to the changes brought about by fluctuating temperature in the distribution of radioactive gases in the atmosphere. Any true fluctuation has an amplitude of less than 0·2%.

Finally, it is not possible to record any real progress towards a decision concerning the origin of the penetrating radiation. The only novel suggestion during the year has been that of L. G. H.

[86] *Z. Physik*, 1931, **72**, 625; *A.*, 1932, 5.
[87] *Ann. Reports*, 1932, **29**, 314.
[88] *Z. Physik*, 1932, **75**, 115; *A.*, 1932, 556.
[89] *Ibid.*, **78**, 668; *Physikal. Z.*, 1933, **34**, 896; *A.*, 1934, 128.
[90] *Z. Physik*, 1934, **87**, 800; *A.*, 343.

Huxley,[91] that the earth, maintained at a high negative potential by electrons emitted from the sun, is able to endow with the observed high energies, through electrostatic attraction, such positively charged particles as happen to be in its neighbourhood. It is doubtful, however, how far such a suggestion will stand the test of further investigation, experimental and theoretical.

N. FEATHER.

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[91] *Nature*, 1934, **134**, 418; *A*., 1152.

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